METAL FINISHING SURVEY

FOR ONTARIO

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METAL FINISHING SURVEY FOR ONTARIO

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Abstract

A survey of the metal finishing industry in Ontario was completed to identify companies which are engaged in this industry, the processes which are conducted, the quantities and types of wastes that are produced and the types of metal finishing operations that are used. Six hundred and ninety-five (695) companies from 1343 active companies responded to a survey.

The total number of companies engaged in metal finishing was estimated at 500 to 700. The most frequently reported operations were electroplating, chemical conversion coating and chemical etching and milling.

The wastes streams can generally be classified as, rinse waters, spent process solutions and sludges. Rinse water is produced at a average rate of less than 379 m^3/day/plant. The most common method of treating it is to precipitate the metals to produce a sludge for disposal. Recycling and recovery of the metal values is practised by 54 companies surveyed. 22% of the companies surveyed reported that they did not treat their rinse waters.

The most common method of treating spent process waste waters is by treatment in the rinse water treatment system. Other techniques included treatment in separate systems and disposal off-site by commercial haulers. The average quantity of spent process solution disposed of in the sanitary sewer was 13,854 m^3/year, to secure landfill was 58 m^3/year and to reclaimers was 53 m^3/year.

Sludge was mainly produced in the waste treatment system at an average rate of 532 m^3/year. It was also produced in rinse and process tanks at an average rate of 17 m^3/year and 10 m^3/year respectively. The most common method of disposing of sludge was in a secure landfill site.

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1.0 EXECUTIVE SUMMARY

The Ontario Ministry of the Environment has become increasingly concerned over the management of wastes in the metal finishing industry in Ontario. Accordingly, a survey of the industry was commissioned to identify companies which are engaged in metal finishing, the processes which are conducted, the quantities and types of waste that are produced and the types of metal finishing operations that are used. A broad definition of metal finishing was adopted for the survey including electroplating, anodizing, chemical conversion coating (colouring, phosphating, passivation and chromating), immersion plating, electroless plating, hot dipping, printed circuit board manufacturing and chemical milling, etching, bright dipping and stripping. A questionnaire was developed, as shown in Appendix A, to gather information from companies involved in metal finishing.

The questionnaire was mailed to a master list of 1,422 companies. Approximately 200 companies were contacted by phone regarding the survey which revealed that 77 were no longer in business. Six hundred and ninety-five (695) or 52% of the 1,343 active companies responded to the survey to identify 262 companies engaged in metal finishing operations. Many of the engaged companies (60) were contacted or contacted Proctor & Redfern regarding the details of the questionnaire. Comments and/or adjustments were added to the submitted forms. In addition, ten plants throughout the province were visited to confirm the results of the survey and to discuss operations in detail. The data gathered from the survey is therefore considered to be representative of the companies surveyed.

The major conclusion of the survey was that the processing operations and wastes generated in the metal finishing industry are complex. Most plants conduct many of the targeted processes and therefore generate waste streams which are both complex in nature and complex to treat. Nevertheless, the wastes can generally be classified as spent process solutions, rinse waters and sludges.

The data from the survey indicated that few companies try to recycle the metal contaminants in rinse waters. The most common method of treating rinse waters which contained primarily metal, as well as organic, contaminants and either acidic or alkaline pH levels, was to precipitate the metals to produce a sludge for disposal. The average quantity of sludge produced was 18,800 ft^3/year by 192 companies which produced sludge in a waste treatment system. Recycling or recovery of metals in rinse water was practised by 54 companies which used evaporation, electrolytic recovery, ion exchange and static rinse recycling techniques. It is worth noting that 22% of the companies surveyed reported that they did not treat rinse waters. Rinse waters were discharged primarily to sanitary sewers at an average rate of less than 379 m^3/day.

Spent process solutions consisted mainly of cleaners and etches. They were disposed of using various techniques, the most common of which was to feed them into the rinse water treatment system. Other techniques included treatment in separate systems and disposal off-site by commercial haulers. The average quantity of spent process solution disposed of to the sanitary sewer was 13,854 m^3/year, to secure landfill was 58 m^3/year and to reclaimers was 53 m^3/year.

Sludge was mainly produced in the waste treatment system as indicated above at an average rate of 532 m^3/year/plant. It was also produced in rinse tanks and process tanks at an average rate of 17 m^3/year and 10 m^3/year respectively. The most common method of disposing of sludge was in a secure landfill site.

The size of metal finishing companies was estimated by the amount of money spent on metals and metal salts in one year. The data was broadly distributed and indicated that 57% could be considered to be small companies which spent less than $50,000/year. Some companies spent as little as $1,000/year while others spent $50,000,000/year.

The most frequently reported metal finishing operations were electroplating, chemical conversion coating and chemical etching and milling. The most frequently reported metals used in finishing operations were zinc, chromic acid, aluminum (as a substrate), nickel, tin and copper.

The data produced in this survey was based on responses by 262 metal finishing companies. Since responses from 52% of the 1,343 active companies were received, it is reasonable to assume that the total number of metal finishing companies could be estimated at approximately 500 companies. However, this number may underestimate the total because many companies which apply a phosphate coating to their products prior to applying paint did not consider themselves to be metal finishing companies. Since this sequence of operations - phosphating then painting - is thought to be very common, the total number of metal finishing companies is estimated at 500 to 700 companies.

The main concern of several companies was that there are no uniform standards for waste treatment in the industry. Dilution is still an acceptable practice to achieve compliance with the concentration limits specified in sewer use by-laws. A loading restriction in kg/day would force the "diluters" to treat wastewaters and bring all metal finishing companies to a common basis for operating costs.

2.0 INTRODUCTION

The Ontario Ministry of the Environment (OMOE) retained the Proctor & Redfern Group to conduct a survey of the metal finishing industry in Ontario. The objective of the survey was to describe the industry in general terms by; listing companies engaged in metal finishing and their location, describing metal finishing processes currently in use; describing waste treatment and disposal methods currently in use.

Data for the survey was generated from a questionnaire that was sent to 1,422 companies. In addition, existing literature was used to supplement technical information on metal finishing processes and waste treatment methods which are described in Appendices B and C respectively.

The methodology used to develop the list of companies engaged in metal finishing activities was complex. It was necessary to try to "discover" the captive metal finishing companies who do not sell a metal finishing service to others but rather use it "in house" as one of many manufacturing steps. The job shops by contrast advertise their service and are therefore more readily identified.

The definition of metal finishing for the purpose of this survey included seven categories of operations. Generally, the finish was applied to metal substrates although some companies were surveyed who plated on plastic since operations associated with applying metals to plastic produce wastes which are very similar to those produced using metal substrates.

The OMOE regulates the disposal of certain wastes produced by the metal finishing industry through Ontario Regulation 309. The various waste streams can be categorized as classified wastes such as Classification 131 for metal finishing waste treatment sludges or by the comprehensive definitions of hazardous industrial wastes and leachate toxic, reactive, corrosive or ignitable wastes.

The data from this survey was used to describe the disposal methods currently used for various metal finishing wastes but does not address the classification of the waste.

This report presents the results of Proctor & Redfern's survey.

3.0 SUMMARY

1. Metal Finishing was defined for this survey as being any one of the operations listed below. Each operation is described in detail in Appendix B.

   a) common and precious metal electroplating
   b) anodizing
   c) chemical conversion coating (colouring, phosphating, passivation, chromating and immersion plating)
   d) electroless plating
   e) chemical etching and milling, bright dipping, stripping or electropolishing
   f) printed circuit board manufacturing
   g) hot dip coating

   A list of 1,422 companies that were potentially engaged in at least one of the above mentioned operations was developed from nine sources.

   The sources are shown below along with the number of metal finishing companies that were identified from each source:

Source	No. of Companies Identified
Scotts Directory - SIC 3471	71
Proctor & Redfern's Files	110
Waste Manifest Data Set	120
Scotts Directory - Group 34 Scan	28
Trade Association Membership	80
Scotts Directory - random screening of major cities	30
Journals, articles, papers	15
Municipality Files	83
Scotts Directory - SIC 3479	22
Total No. of Metal Finishing Companies	262

A questionnaire (shown in Appendix A) was developed and sent to the 1,422 companies. Approximately 200 companies were contacted regarding the survey which revealed that seventy-nine (79) companies were no longer in business. Responses from 52% (695) of the 1,343 active companies were received, of which 262 were engaged in metal finishing as defined for this survey. The data from the 262 respondents was analysed to describe the metal finishing industry in Ontario.

2. The most common metal finishing operations were found to be electroplating, chemical conversion coating and chemical etching, milling, bright dipping, stripping and electropolishing, being defined as operations by 64% (168), 60% (158) and 46% (121) of respondents respectively (Table 1).

   The data also revealed that most companies are involved in more than one metal finishing operation.

3. The size of metal finishing companies was estimated by the amount of money spent to buy metals and metal salts. More than half of the companies (57%) could be considered small because they spent $50,000/year or less on metals and metal salts (Table 2).

4. The most common electroplating operations performed in 168 plants were copper, nickel, chromium and non-cyanide zinc being reported by 85, 93, 65 and 36 of the electroplaters respectively (Table 3). Racks were the most common method of handling parts (341) followed by barrels (124). The 168 electroplating plants operated 493 baths and treated rinse waters from 370 of those baths.

5. The most common electroless plating operations performed in 49 plants were nickel and copper (Table 4). Racks were the most common method of handling parts (49). The 49 plants operated 59 baths and treated rinse water from 39 baths.

6. The most common immersion plating operations at 28 plants were nickel on steel, copper on steel, chromium on steel and tin on copper. A total of 35 plate - substrate combinations were reported. Racks were the most common method of handling parts. Thirteen of the 28 plants treated rinse waters.

7. The most common phosphate coatings were iron and zinc phosphate in the 81 plants conducting phosphating. Racks were the most common method of handling parts (54 plants). Rinse water was treated by 63 plants.

8. The most common colouring operations reported by 29 plants were based on chromating, oxidizing, painting or phosphating. Racks were the most common method of handling parts. Rinse water was treated by 19 plants.

9. The most common passivation operations performed in 31 plants were based on chromate solutions or acid solutions applied to stainless steel. Racks were the most common method of handling parts (33). Rinse water was treated in 22 plants.

10. The most common use of chromating operations performed in 58 plants was for sealing zinc plated parts to prevent oxidation (Table 5). Racks were the most common method of handling parts (33). Rinse water was treated by 42 plants operating 116 baths.

11. The most common hot dipping operations performed in 26 plants were zinc and tin on steel (Table 6). Racks were the most common parts handling method (13). Rinse water was treated at 15 plants. Two plants reported recycling static rinse water and using off-site disposal companies to achieve zero discharge.

12. The most common anodizing operation, performed in 38 plants, was the anodizing of aluminum (Table 7). Magnesium and zinc anodizing were rare. Racks were the most common method of handling parts (29). Rinse water was treated at 24 plants.

13. The most common milling and etching operations, performed at 62 plants, involved the use of ferric chloride and caustic baths (Table 8). Racks were most commonly used to handle parts. Rinse water were treated by 38 plants.

14. Bright dipping operations were performed at 72 plants (Table 8). The most common metals treated were copper and aluminum. Racks and barrels were used to handle parts. Rinse waters were treated at 37 plants.

15. Stripping operations were conducted at 47 plants (Table 8). The most common metals stripped were nickel, chromium, solder, gold, copper and brass. Racks were most commonly used to handle parts. Rinse waters were treated at 37 plants.

16. The most common electropolishing operation, reported in 9 plants, was on a stainless steel substrate (Table 8). Racks were the most common method of handling parts. Rinse water was treated in 6 plants.

17. Methods to reduce water usage were used by 199 respondents (Table 9). The most common techniques were:

    a) counter current rinsing (120)
    b) longer withdrawal/drainage times (98)
    c) spray rinsing (93)
    d) flow restrictors (76)
    e) reusing contaminated rinse water and treated effluent (70)

    The various waste treatment methods reported in Summary items 17 through 23 are described in detail in Appendix C.

18. Methods to treat rinse waters were implemented by 184 respondents (Table 10). The most common treatment systems produce a sludge for disposal since neutralization, precipitation, gravity settling and filtration were reported to be used by 141, 88, 105 and 91 respondents respectively. Techniques to allow the recycling or recovery of metals such as evaporation, electrolytic recovery and possible ion exchange were reported less frequently.

19. The data from 248 respondents indicated that 91% of plants used less than 379 m^3/day (Figure 3). The discharge points for wastewaters were (Figure 4):

sanitary sewer	82%
storm sewer	7%
lake or stream	1%

Five companies reported that wastewaters were totally recycled or reused. Four reported using septic tank systems.

20. Spent process solutions were most commonly disposed of in on-site treatment plants (145) or hauled off-site (140) (Figure 5). The practice of sending spent process solutions to reclaimers (56), discharging directly to sanitary sewer (31) and others (16) were less common. The most commonly disposed of process solution was the alkaline and acid cleaners.

The average volume discharged to the sanitary sewer was 13,854 m^3/year over the 121 plants using this disposal route (Figure 6). The average volumes discharged to landfill, and reclaimers were 58 and 53 m^3/year respectively.

Many specialized treatment methods were described and are presented in Section 7.2.7.

21. The largest quantities of sludge were produced from wastewater treatment plants averaging 532 m^3/year over the 192 plants responding to the question (Figure 7). Rinse tanks and process tanks produced an average of 17 m^3/year and 10 m^3/year respectively.

    Sludge was disposed of in secure landfill sites (111), municipal landfill sites (37), recycling companies (34), Falconbridge Ltd (6) and Foundries (3) (Figure 8).

22. The six metals that were purchased in the largest quantities were zinc, chromic acid, aluminum (metal to be finished), nickel, tin and copper (Table 11 and Section 7.2.9).

23. Cyanide based electroplating operations were being conducted by 68 plants but only 48 of these plants reported using cyanide destruction in their rinse water treatment processes.

24. The geographic distribution of the metal finishing plants in Ontario identified by this survey is shown in Figure 1.

25. Visits to 10 metal finishing plants revealed the questionnaires were generally filled out properly and that;

    a) some companies who operated captive shops were actively seeking methods of getting out of the business,

    b) most companies were aware of regulations regarding wastewater quality, and waste disposal,

    c) smaller sized shops used commercial, off-site services to control wastes rather than invest in an in-house pollution control system.

d) several plant managers commented that a loading restriction based on kg of metal pollutant per day rather than a concentration restriction in milligrams/litre was required to ensure that all metal finishing companies would treat wastewaters. They believed that too many companies were avoiding the costs of treating wastewaters by diluting them to comply with sewer use by-laws and therefore "legally" obtained a cost advantage in a very competitive business. This survey shows that 52 plants do not treat wastewaters.

The plant visits were conducted in London, St. Catharines, Newmarket, Scarborough, Peterborough, Toronto, Downsview, Mississauga, Thunder Bay and Whitby.

4.0 CONCLUSIONS

1. The metal finishing industry is a very complex industry from the point of view of the number of recorded and potential processes which are used in each plant. This suggests that the management of the many and varied types of waste is also complex. While the data from 262 plants has produced an overview of the industry in reasonable detail, more indepth analysis would be required to categorize and describe the "mass balances" in sufficient detail to support changes to the legislation aimed at controlling wastes, particularly to set loading restrictions on discharges to sanitary sewers and to specify sludge disposal routes to secure or municipal landfill sites.

2. The response to the questionnaire was very good at 52%. However, it appears that there are likely to be 500 to 700 or more metal finishing companies in Ontario. This survey has developed a list of 262 metal finishing companies which therefore represent about 38 to 52% of those engaged in the industry.

3. Many companies which telephoned to discuss the questionnaire prior to completing it were not certain that they should be classified as a metal finishing companies. Most of these companies were conducting phosphating operations prior to painting their products. Since many companies are thought to use this process, more emphasis should be placed on phosphating/painting during any subsequent survey work.

4. A relatively large number of plants (52) report that they did not treat rinse waters. Presumably, they used sufficient dilution to achieve compliance with local sewer use by-laws. In view of the proposed new strategies for waste management, loading restrictions would force the "diluters" to treat rinse waters. In fact, this was the major complaint of those practising wastewater treatment. A uniform set of standards for treatment was stated to be necessary in order to bring all metal finishing companies to a common basis, particularly an operating cost basis, so that all companies would be competing equally.

5.0 RECOMMENDATIONS

1. Develop a more comprehensive and detailed chemical description of metal finishing wastes and their appropriate disposal routes by conducting an extensive sampling and testing program of actual wastes samples to support changes to the legislation. The program should be conducted on the metal finishing companies identified in this survey since they are thought to represent a good cross-section of the industry.

2. The OMOE should communicate the definitions of metal finishing to industry in Ontario, requesting that companies identify themselves as metal finishing companies, if appropriate.

3. Standards for the discharge of various pollutants on a loading as well as a concentration basis should be developed and enforced by the OMOE to bring the industry to a common basis of operation. Data to support this program could be generated by the work described by recommendation 1.

4. Metal finishing should be defined as any one of the 7 operations described in this survey when applied to any substrate including plastics, metals or other material.

5. Some additional work should be done to identify companies who phosphate parts prior to painting using the techniques employed in this survey, since they are thought to be large in number and do not generally consider themselves to be electroplaters.

6.0 METHODOLOGY

6.1 Introduction

This section describes the methodology or techniques employed to conduct the survey. The following subsections describe the techniques used to develop the list of companies engaged in metal finishing and the development of the questionnaire and the strategy used to follow-up contacts by phone and the program of plant visits.

6.2 List of Metal Finishing Companies

The definition of metal finishing, as defined in the Terms of Reference from OMOE, is any one of the following operations, which are described in detail in Appendix B:

a) common and precious metal electroplating,
b) anodizing,
c) chemical conversion coating (e.g. colouring, phosphating, passivation, chromating and immersion plating),
d) electroless plating,
e) chemical etching and milling, bright dipping, stripping or electropolishing,
f) printed circuit board manufacturing,
g) hot dipped coating (e.g. galvanizing).

In general, it was assumed that the substrate being finished was a metal. However, plating on plastic is becoming more common, particularly for automotive trim and other decorative applications such as plumbing fixtures. The processes and wastes generated are very similar to the metal substrate equivalent and therefore, some companies plating on plastic were included in the work program.

Metal finishing companies can be generally categorized as job shop or captive. Job shops offer metal finishing services to the public. For example, one company conducts nickel and chromium plating on virtually any small to medium sized part that can be handled by their equipment. Captive metal finishing companies conduct one or more metal finishing operations "in-house" as one of many manufacturing steps. For example, one company applied a zinc coating electrolytically to steel housings for small electrical parts.

The problem of identifying which companies are engaged in metal finishing, either as a job shop or as a captive user, is complex. Large job shops advertise their services. However, many companies are small, do not advertise and are therefore difficult to identify. Captive shops do not identify themselves as metal finishing companies since it is typically a small portion of the overall operation.

Many sources were used to identify a master list of metal finishing companies including the following:

i) Waste Manifest Data Set,
ii) Proctor & Redfern Files
iii) Scotts Directory,
iv) Trade Associations,
v) Regional Municipalities,
vi) Other sources.

The method of using each source is described below.

6.2.1 Waste Manifest Data Set (1987)

The Waste Manifest Data Set (1987) was searched under four classifications to identify generators of wastes which are common in metal finishing operations. Classifications 112 (acid waste-heavy metal), 121 (alkaline waste-heavy metal), 123 (alkaline phosphate) and 131 (neutralized waste-heavy metals) produced a listing of generators who manifested wastes that could have been produced by metal finishing companies. This list contained 120 metal finishing companies.

6.2.2 Scotts Directory

Scotts Directory is a listing of companies by the Standard Industrial Classification (SIC) code. Many companies register with Scotts under their primary function only. Thus, larger job shop metal finishing companies list under code 3471 (electroplating, plating, polishing, anodizing and colouring) or possibly under 3479 (coating, engraving and allied services, not elsewhere classified). Companies under the 3471 and 3479 codes contained 71 and 22 metal finishing companies respectively.

Captive metal finishing companies register under their primary function which was not metal finishing. While it is possible to register secondary and tertiary functions in Scotts, which could be a metal finishing code such as 3471, no such listings were found. No captive metal finishing companies were found under the secondary SIC designation.

Scotts Directory is also organized by city. A manual search of 27 major cities was made to identify potential metal finishing companies by the name of the company, by association with other known metal finishing companies or by general knowledge. The cities searched included Bancroft, Barrie, Brantford, Cambridge, Guelph, Halton Hills, Hamilton, Hannon, Hanover, Kingsville, Kirkland Lake, Kitchener, London, Organeville, Orillia, Port Colbourne, Port Elgin, Port Hope, St. Catharines, St. Thomas, Sarnia, Stoney Creek, Strathroy, Sudbury, Waterloo, Whitby and Windsor. This list contained 30 metal finishing companies.

Scotts Directory was also searched under SIC code 3401 - 3499 which was thought to contain metal finishing companies. This list produced 200 names, excluding the 3479 and 3471 categories, which contained 28 metal finishing companies.

6.2.3 Trade Associations

Ontario has many trade associations. Those which were found to represent metal finishing companies are listed below:

- Die Casters Association in Ontario,
- Motor Vehicle Manufacturer's Association in Ontario,
- Canadian Copper & Brass Development Association,
- Ontario Foundry Association,
- Canadian Steel Environmental Association,
- Architectural Aluminum Anodizers Group,
- Canadian Association of Metal Finishing companies (founded in 1989),
- Electrical & Electronic Manufacturer's Association of Canada (includes Canadian Appliance Manufacturers Association of Canada, Portable Appliance Manufacturers Association of Canada, and Consumer Electronics Marketers of Canada).
- Automotive Parts Manufacturing Association.

Each association was contacted and asked to provide a membership list. All the submitted names were included in the master list of potential metal finishing companies. Where membership lists were not supplied by the association, questionnaires were supplied by Proctor & Redfern and distributed by the association. These lists contained 80 metal finishing companies.

6.2.4 Regional Municipalities

The Municipalities of Peel, Niagara, Toronto and Kitchener-Waterloo were each asked to submit lists of metal finishing companies in their jurisdictions. The company names were added to the master list for the project. These lists contained 83 of the metal finishing companies.

6.2.5 Proctor & Redfern Files

The Proctor & Redfern Group has been involved in the waste management field for many years. A list of company names was added to the master file for the project which contained 110 metal finishing companies.

6.2.6 Journals, Articles, Papers and Others

A list of company names was compiled from various sources including journals, articles, newspaper, telephone books, equipment supplies and chemical suppliers. This list contained 15 metal finishing companies.

6.3 Questionnaire

The major source of data for describing the metal finishing industry in Ontario was the questionnaire shown in Appendix A. It was developed to gain information from each company on the following topics:

- name of the company,
- size of the company,
- types of metal finishing operations conducted,
- methods of controlling water usage,
- methods of treating rinse water,
- volume and disposal route for treated rinse water,
- methods of treating spent process solutions,
- quantity and disposal route for sludges,
- quantity of metals, metal salts or acids used,
- brief description of the companies area of business.

Definition

The questions and answers were designed to produce information that was sufficiently detailed to describe general operations without requiring a lot of time to complete. Accordingly, most questions could be answered with a single word, symbol or check mark.

The definition of each of the metal finishing operations used in the survey was indicated on the questionnaire, as shown in Appendix A. For example, electroplating is defined as "the deposition of a thin layer of a metal from a solution onto a substrate by the use of an electric current (electrodeposition)". The definitions were included in the questionnaire to avoid confusion over what was meant by each term.

The questionnaire was reviewed by the project staff at the MOE prior to being issued. It was also submitted to the directors of the trade associations for their comments prior to being issued. Most replied with constructive comments and offered to encourage their members to complete the questionnaire by contacting them directly or through the use of regular communications literature.

6.4 Follow-up Contacts

A general program of follow-up contacts was instituted to enhance the responses to the questionnaire. The approach was to contact about 200 of the companies which did not respond to the questionnaire to ask that it be completed. Approximately 50 additional metal finishing companies were identified by this effort and 77 companies were found to be inactive. In addition, as each completed questionnaire was received, it was reviewed. Approximately 60 companies were contacted to confirm the data presented which was usually correctly presented. Any discrepancies have been included in the results.

Many companies were not sure if they should be classified as a metal finishing company using the definitions in the survey. This was particularly true of those

engaged in phosphating prior to painting their products. More emphasis should be placed on phosphating/painting in any subsequent survey.

6.5 Plant Visits

The contents of some questionnaires were further confirmed by conducting tours at 10 of the plants engaged in metal finishing operations. The plant visit allowed the collection of more detailed information on processing and waste management activities and provided the opportunity to discuss various aspects of the industry.

The selection of ten metal finishing plants to visit was based on the following factors as described below:

a) Geographic Location:

Plants were visited in all active cities of the province including London, St. Catharines, Newmarket, Scarborough, Peterborough, Toronto, Downsview, Mississauga, Thunder Bay and Whitby.

b) Metal Finishing Operations:

Plants were visited to witness as many metal finishing operations as possible including: printed circuit board manufacturing; zinc, nickel, copper and chromium electroplating on steel and plastic using both racks and barrels; brush electroplating and anodizing.

c) Wastewater Treatment Operations:

Plants were visited to witness as many types of wastewater treatment operations as possible including: ion exchange/precipitation treatment; ultrafiltration; cyanide destruction; electrolytic recovery; hexavalent chromium reduction and standard neutralization, precipitation, settling and filtering.

d) Company Size and Type:

Plants were selected for a visit based on size. Generally they were purchasing $50,000 to $500,000 worth of metal salts or metals per year but one was very small spending only $5,000/yr and one was large spending $1,900,000/yr. Five were captive shops and five were job shops. One company plated on plastic while nine finished metal substrates.

7.0 RESULT OF THE SURVEY

7.1 Introduction

The questionnaire shown in Appendix A was sent to 1,422 plants in Ontario that were either known, or thought to be conducting metal finishing operations. Seventy nine of these plants were found to be closed, leaving 1,343 active plants. Amongst them, 695 or 52% responded to the survey, of which 262 or 38% were engaged in metal finishing. The data from the 262 plants was analysed to provide the basis for the description of the metal finishing industry in Ontario. The answers to each question in the questionnaire are summarized in the sections below. Additional analysis of the data is presented in Section 7.3

A detailed description of the metal finishing operations that are the being considered in this report are described in Appendix B of this report. A detailed description of common waste treatment processes is provided in Appendix C. The reader should consult these Appendices when more information is required.

7.2 Summary of Responses to the Questionnaire

7.2.1 Types of Metal Finishing Operations (Question 1)

Overall, 262 plants were found to be involved in one or more of the identified metal finishing operations. The number of plants involved in each metal finishing operation is shown in Table 1.

The data shows that the most common metal finishing operations are:

- Electroplating
- Chemical Conversion Coating
- Chemical Etching, Milling, Bright Dipping, Stripping or Electropolishing

They were identified as operations by 168, 158 and 121 plants respectively.

The data from question 1 was also analysed to determine how many plants were dedicated to only one category of metal finishing. Table 1 shows that 104 or 40% of the plants were dedicated to one category of operation, mostly those involved in electroplating and conversion coating. The remaining 60% of the plants were involved in more than one operation. This data may be somewhat misleading, however, since, for example, virtually all electroplaters do some stripping of metals that build up on plating racks or that have produced "off-spec" finishes. A similar argument may apply to those involved in conversion coating. The general conclusion is that most companies involved in metal finishing tend to be involved in more than one operation.

7.2.2 Size of Metal Finishing Companies (Question 2)

The size of metal finishing companies was estimated by asking for the amount of money spent on metals or metal salts in one year. This quantity fairly reflects the volume of finishing activity in a general sense. It was also considered to be less sensitive information than gross sales or profit and therefore more likely to be reported.

Two hundred and three (203) companies out of 262 responded to the question. The data, summarized in Table 2, and shown in Figure 2, shows that the amount of money spent ranges from <$1,000 to >$10,000,000. Furthermore, 86% of the companies spend $500,000 or less on metals and metal salts and that 58% can be considered small companies spending $50,000 or less. This data tends to support the theory that there are a few large companies and that there are many smaller operations.

7.2.3 Detailed Metal Finishing Operations (Question 3a to 3g)

Each of the metal finishing operations are described in the following sections by metal type, parts handling methods and whether or not rinse water is treated. Handling methods for parts are shown as rack (R), coil (C), barrel (B) or other (O) handling methods. (Coil refers to a metal finishing operation being applied to a coil of wire or flat metal stock. The stock is fed continuously through the baths to apply the finish). Some companies used several handling methods for

one type of metal finishing, for example, nickel plating using both racks and barrels.

7.2.3.1 Electroplating (Question 3a)(ref. Appendix B, Section 2.0)

The number of plants engaged in each of the metals in the questionnaire are summarized in Table 3. The breakdown of handling methods used and whether or not rinse water was treated are also shown in Table 3. Electroplating of copper (both non-cyanide and cyanide), nickel (both watts and sulfamate), chromium and non-cyanide zinc were most common. A large number of plants also electroplated brass, cadmium cyanide, aluminum, lead-tin, alkaline stannate, stannous sulfate, nickel-tin, zinc cyanide, gold (both cyanide and non-cyanide), silver and rhodium. Electroplating of bronze, non-cyanide cadmium, iron, lead, stannous fluoborate, tin-copper alloy, tin-zinc alloy, palladium (both non-cyanide and cyanide), platinum, indium, and ruthenium was rare. No plants were engaged in iridium or osmium electroplating.

The majority of plants (341) handled parts using racks which produced less dragout than handled by barrels (124). Electroplating of coil stock was much less common (31). This was true for most metals but not all. For example, parts being zinc electroplated were mostly handled in barrels.

Table 3 also shows the number of electroplating bath types that were used and the number of bath types which treated the rinse water. For example, brass plating was carried out by 22 plants but only 21 reported that rinse waters from the bath were treated.

The "Total number of operations" line in Table 3 shows that the 168 companies involved in electroplating operated 493 baths, treated rinse waters from 370 baths and did not treat rinse waters from 123 of those baths. The fact that rinse waters were not

treated may imply that they were discharged directly, stored for disposal off-site or recycled. In any case a large percentage of the rinse water streams may require treatment.

7.2.3.2 Electroless Plating (Question 3b)(ref. Appendix B, Section 5.0)

There were 49 plants which were engaged in electroless plating. Table 4 shows that electroless plating of nickel and copper were the most common. A few plants were involved in gold, palladium, arsenic, chromic acid, silver, tin, nickel sulfate and titanium electroless plating. None were engaged in electroless plating with iron, chromium alkaline, brass or bronze.

Parts were most commonly handled using racks (49). Some plants also used barrels (8) or plated coils (4).

The "Total number of operations" line in Table 4 shown that the 49 companies involved in electroless plating operated 59 baths, treated rinse waters from 39 baths, and did not treat rinse waters from 20 baths. Similar to electroplating operations, a substantial number of rinse waters may require further treatment.

7.2.3.3 Immersion Plating (Question 3c)(ref. Appendix B, Section 3.0)

There were 28 plants which conducted immersion plating. Thirty five combinations of plating metal and substrate were reported. Nickel on steel, copper on steel, chrome on steel and tin on copper were most common operations. All others were either unique or had only one duplicate. Examples of them include copper on nickel, silver on lacquer, chrome on brass, etc.

Rack plating was used in 24 applications, coil was treated in eight and barrels in nine applications. Thirteen out of the 28 plants

treated rinse water used in the immersion plating operation while 15 did not treat rinse water.

7.2.3.4 Chemical Conversion Coating (Question 3d)
(ref. Appendix B, Section 4.0)

Chemical conversion coating involves the processes of phosphating, colouring, passivation and chromating. One hundred and fifty eight plants were involved in one or more of these operations. The results of the survey are described below:

Phosphating

Eighty one plants were involved in phosphating. Sixty one of them gave details or comments. The majority were involved in iron or zinc phosphating. Some manganese phosphating and rare cases of chrome phosphating were also reported. The substrate was mostly steel. Aluminum as a substrate was sometimes observed. Phosphating was used by several plants as a surface preparation technique before painting or colouring.

Parts were primarily handled on racks (54 plants) while 18 used barrels and 7 treat coils of stock.

Sixty three of the 81 plants treated their rinse water used in phosphating operations while 18 plants did not treat their rinse waters.

Colouring

Twenty nine plants were engaged in colouring operations. Twenty five of these companies reported that colouring was achieved by chromating, oxidizing, painting, dying or phosphating processes. Substrate metals included aluminum, cadmium, brass, bronze, and stainless steel with aluminum being the most common.

The number of plants which handled parts by rack, coil and barrel were 21, 1 and 5 respectively.

Nineteen out of the 29 plants treated rinse water used in the colouring processes while 10 did not treat rinse water.

Passivation

Thirty one plants were engaged in passivation. Data from twenty five of these companies showed that passivation was normally conducted using an acid or a chromate solution. The acid solutions were primarily nitric acid or a proprietary solution of perchloric, hydrofluoric, chromic and phosphoric acids. The chromate solution consisted of nitric, dichromate, hexavalent chrome or others. The substrate metal passivated was most commonly stainless steel. Brass parts were passivated in one plant.

The number of plants which handled parts by rack, coil and barrel were 19, 2 and 9 respectively. Twenty two of the 31 plants treated rinse water used to rinse passivated substrates while 9 did not treat rinse water.

Chromating

Chromating was reported as a metal finishing operation by 58 plants, as shown in Table 5. The most common use of the chromating operation (38 plants) was for sealing rinses on zinc plated parts to prevent oxidation (white rust). Many formulations were reported including dilute chromic acid, potassium dichromate, sodium dichromate and various proprietary baths. Other reported chromating operations included black oxidizing on steel, bright chrome, brass and copper plus the application of yellow and blue chromium colours. Four plants reported the use of cyanide bearing chromating solutions.

The most common parts handling method was using racks or barrels. Chromating of coil stock was rare.

Rinse water was treated at 42 out of the 58 baths reported while 16 did not treat rinse water.

7.2.3.5 Hot Dipping (Question 3e)(ref. Appendix B, Section 7.0)

Hot Dipping was reported as a metal finishing operation by 26 plants as shown in Table 6. Zinc and tin were the most commonly applied finishes being indicated by 10 plants each. Lead was applied at 6 plants and aluminum was applied at 2 plants.

The most common parts handling method was using racks (13) while coil stock was used by 6 plants, barrels used at 2 plants and other methods such as slings were used at 6 plants.

Rinse water was treated at 15 out of 28 baths while 13 did not treat rinse water. Section 7.2.6 describes two hot dip galvanizing plants which do not treat wastewater but use recycling and off-site disposal to achieve zero discharge.

7.2.3.6 Anodizing (Question 3f)(ref. Appendix B, Section 6.0)

Anodizing was reported as a metal finishing operation by 38 plants as shown in Table 7. Aluminum was the most commonly anodized substrate (30 plants). Magnesium and zinc anodizing were reported by 1 and 2 plants respectively. Titanium anodizing was not reported.

The most common parts handling method was using racks (29) while barrels were reported once and coil stock treatment 3 times.

Rinse water was treated at 24 out of 33 baths while 9 did not treat rinse water.

7.2.3.7 Chemical Milling, Etching and Bright Dipping (Question 3g) (ref. Appendix B, Section 8.0 and 9.0)

Detailed milling, etching and bright dipping activities are illustrated in Table 8.

Milling and Etching

A wide variety of other baths were used in milling and etching. They included various pure and mixed acids, ammoniacal etchant and caustic alkaline etchant. The most commonly used pure acids were nitric, hydrochloric and hydrofluoric acid. Mixed acids included phosphoric-nitric, hydrofluoric-nitric, peroxide-sulfuric, etc. Ammoniacal etchants included ammonium chloride, fluoride and hydroxide.

Bright Dipping

There were nine plants involved in other types of bright dipping. Five of these plants performed bright dipping of brass. The others were titanium, stainless steel, metallic glass, nickel and iron carbon steel. The use of phosphoric acid was indicated by one plant.

Stripping

There are 47 plants involved in stripping operation. A vast variety of metals were stripped. More common ones included nickel, chrome, solder, gold, copper and brass in decreasing order. Zinc, cadmium, lead, aluminum, organic paint, zinc-tin and tin were also stripped by few plants. Steel parts were generally stripped for

rework. Various acids, caustics, ammonium bifluoride, hydrogen peroxide solution, or proprietary strippers were used.

Electropolishing

Various acids including phosphoric, hydrochloric and hydrofluoric acid were used for electropolishing. Metals being polished were stainless steel, nickel, aluminum, iron carbon steel, or metallic glass. Stainless steel was the most common one.

Others

There were two plants engaged in other types of activities. One was grinding and polishing of type 300 to 400 stainless steel. The other was buffing of aluminum.

7.2.4 Water Reduction Measures (Question 4)(ref. Appendix C, Section 2.0)

Metal finishing operations require large quantities of water to rinse parts between the individual processing steps. Water usage rates and costs can be greatly reduced by several proven techniques. Moreover, reducing the volume of wastewater requiring treatment decreases the capital, and in some cases the operating cost, of wastewater treatment systems. The data accumulated from Question 4 in the questionnaire is summarized in Table 9 and discussed below.

Water reduction measures have been instituted by 199 of the 262 respondents, were being planned by 17 others, were not being used by 37, and 9 did not respond. Counter flow rinsing was the most common technique (120 plants). It is a method which employs several rinse tanks in series, positioned after a process bath. Rinse water flows from one tank to the next, usually by gravity. It flows in the opposite direction to the work and becomes more concentrated as it approaches the first rinse tank. The work is immersed in each successive rinse tank, becoming cleaner and cleaner as it reaches the final rinse tank. The final

rinse tank is fed with fresh or uncontaminated water. Four rinse tanks in series can reduce water consumption by an estimated 70%.

Spray rinsing techniques were reported to be used by 93 plants. Spray rinsing washes parts of processing solutions by spraying them with water rather than immersing them in a tank full of water. The spraying solution may be part of a counter current arrangement, may be fresh water only or a combination of both. Frequently parts are sprayed with fresh water as they are removed from an immersion type of rinsing bath.

Conductivity cells were reported to be used by 22 plants to control the flow rate of rinse water. A conductivity cell can be used to infer the concentration of a contaminant in the final rinse tank. The flow rate of uncontaminated water to the final rinse tank is controlled by the conductivity meter and flow controller to maintain a preset level. Thus the amount of water added is only sufficient to maintain the desired concentration of contaminant in the final rinse tank, thereby minimizing water usage while ensuring that the work is properly rinsed.

Flow restrictors were reported to be used by 76 plants to control water usage. A flow restrictor is a non-adjustable device for controlling water flow rate into the final rinse tank. Experimentation determines the flow setting required to maintain the required concentration of contaminant in the final rinse tank. The advantage to the device is that it cannot easily be "adjusted" so that constant flowrates to treatment systems can be maintained and a consistent quality of rinsing can be achieved.

Dragout minimization was reported to be used by 139 plants : 98 used longer drainage/withdrawal times and 41 used wetting agents. Longer drainage times minimize dragout by allowing more time for the parts to drain over the tank from which they were withdrawn. This minimizes the amount of carry-over into the next bath and can reduce water usage rates. It also can reduce cross-contamination between process tanks by maintaining less contaminated rinses for the same rinse water flow rate. A similar effect can be achieved by lengthening the time required to withdraw the parts from a bath; that is more solution drains back to the bath so that less is carried over to the next bath.

These techniques are most easily applied to automated equipment but can also be effective in manually operated lines.

Wetting agents are used to reduce the surface tension of process baths. They may improve the performance of the bath (such as alkaline cleaners) but also serve to minimize dragout by causing the parts to drain more quickly and more completely.

Water usage was reported to be reduced by reusing contaminated rinse water or treated effluent by 70 plants. One of the most advanced techniques is to treat some of the rinse waters with activated carbon and cation/anion exchangers to remove all the organic, metallic and ionic contaminants. The purified water is then recycled back to the rinse tanks. Regenerant solutions from the ion exchange beds is then treated with normal techniques to precipitate the contaminants. This system offers the advantage of reducing rinse water consumption by 70 to 90% and reducing the capital cost of the wastewater treatment system by minimizing the volume to be treated.

The following additional methods of reducing water consumption were reported by 37 respondents in the "other" category.

i)	Reuse	-	use cooling water as rinse water.
ii)	Control	-	install automatic control valves;
		-	install computerized monitoring systems.
iii)	Rinsing	-	closed loop systems;
	Methods	-	rinse off concentrated solutions over the process tank to replace evaporation/dragout losses.
iv)	Operating	-	turn off the water at night;
	Techniques	-	select parts that drain well;
		-	use smaller batches;
		-	use cooler electrolytes;
		-	install a deionized water system to eliminate flushing before startup;

- use air jets to blow process solutions off the work;
- use dry-in-place equipment to eliminate rinsing (limited applications).

7.2.5 Rinse Water Treatment Methods (Question 5) (ref. Appendix C, Section 3.0)

The common methods for treating rinse waters are described in detail in Appendix C of this report. Table 10 summarizes the results of the survey for Question 5. Overall 184 plants reported that rinse water treatment was conducted, 15 reported that new systems were planned and 52 reported that no treatment was being conducted. The data in Table 10 suggests that waste treatment methods which produce a sludge for disposal are the most common since neutralization, precipitation, gravity settling and filtration were reported to be used by 141, 88, 105 and 91 plants respectively. Techniques which would allow the recycling and/or recovery of metals were less frequently reported. For example evaporation, electrolytic recovery and possibly ion exchange were reported only 24, 18 and 10 times respectively. Similarly, ultrafiltration, which can dramatically increase the operating life of alkaline cleaning baths, was reported only twice.

The respondents indicated that several other technologies were being used namely:

- recovery of metal oxides from baths by filtration;
- micro filtration;
- cyanide treatment by SO_2/air oxidation;
- flocculation and skimming of paint residues;
- skimming floating solids.

The data from Question 3a was analysed to determine that there were 68 plants operating cyanide based electroplating baths. The data from Question 5 revealed that 20 of the 68 plants did not list cyanide destruction as one of the rinse water treatment operations.

7.2.6 Quantities and Destinations of Wastewater (Question 6)

The quantity and destination of wastewaters disposed of by metal finishing companies was estimated from the results of questions 6a and 6b. The data presented in Figure 3, shows that the majority of companies discharge less than 379 cubic metres/day. The few plants (18) who discharge more than 379 cubic metres/day were very large operations.

Five companies reported that wastewaters were totally recycled resulting in a zero discharge rates. Two companies galvanize pipe (hot dip zinc) and achieve zero discharge by: reusing static acid and cleaner rinses for fresh bath makeup, air drying parts after the chromic acid sealing rinse and employing waste haulers to dispose of spent cleaners, acids and rinse solutions (when needed). A third company applies tin to copper using a hot dip process that requires no final rinsing and parts are buffed rather than etched for the initial cleaning. A fourth company applies a ferric oxide colour coating to castings which then air dry. A fifth company chrome plates small parts in a very small system on an infrequent basis. Parts are nickel plated by others. Static rinses in series are used to replace evaporation losses and eliminate water discharges.

Figure 4 presents the survey data describing the discharge point for wastewaters. The majority of the companies (216 or 82%) reported discharging to the sanitary sewer. Twenty-one companies reported that they discharged to the storm sewer (18) or directly to a lake or stream (3). In the "Other" category, some discharged to septic tanks (4) and reused or recycled wastewater (3) instead of discharging.

7.2.7 Spent Process Solutions (Question 7a, 7b and 7c)

The disposal route, destination quantity and treatment methods for process solutions was estimated from the results of questions 7a, 7b and 7c.

The disposal routes for spent process solutions by 244 respondents are shown in summary in Figure 5. It shows that:

i) 31 (or 13%) plants disposed of spent process solutions directly to the sanitary sewer,
ii) 145 (or 59%) plants treated the solutions on-site prior to disposal,
iii) 56 (or 23%) plants reclaimed the solutions for re-use,
iv) 140 (or 57%) plants employed commercial companies to dispose of spent process solutions,
v) 16 (or 7%) plants reported other disposal routes including returning spent baths to suppliers, storage on-site and re-use.

Multiple disposal routes were used by a large number of plants. The average volume of spent process solutions that was discharged to the sanitary sewer system was 13,854 cubic metres/year, as shown in Figure 6, for 124 plants who employed this method of disposal. Secure landfill was used by 46 plants to dispose of an average of 58 cubic metres/year. Spent process solutions were sent to reclaimers by 63 plants to dispose of an average of 53 cubic metres/year. The reason for the large quantity of solutions disposed of in the sanitary sewer is thought to be that respondents included cleaning solutions in their estimates. Soak cleaners, electrocleaners, acid cleaners, etc., require frequent replacement to remain active.

The on-site treatment of spent process solutions was reported by 159 plants. Many plants (104) reported that the solutions were treated by being fed into the rinse water treatment plant.

A wide variety of specialized treatment methods were reported by individual plants as described below:

a) solutions containing gold, silver and rhodium were sent to a metal refining company to recover the valuable metals.

b) a solution containing phosphoric acid was sold back to the supplier.

c) a sulfuric acid pickling solution was treated to recover ferrous sulphate crystals for sale.

d) a process solution was evaporated to dryness to produce a solid waste that was sold for its metal content.

e) metal bearing solutions were sold as raw materials.

f) spent alkaline cleaner was sold as a raw material for pH adjustment.

g) an etching solution was treated to remove aluminum tri-hydrate precipitate and recover the caustic soda etch solution.

h) spent alkaline and acid cleaners were neutralized in separate systems prior to disposal.

i) spent alkaline cleaners were treated with ultrafiltration to remove oil then used to raise the pH in the water treatment system.

j) a spent phosphoric solution was sold to a fertilizer manufacturer.

k) spent copper etching solution was regenerated by the supplier and returned to the user.

l) spent solutions were held in storage.

m) gold from spent baths was recovered by ion exchange and the resin was sent to a reclaimer.

n) a spray dryer was used to produce a solid residue from spent solutions in a zinc galvanizing plant.

o) silver was recovered from photographic developer solutions and sold to a reclaimer.

p) spent phosphate solutions were treated with calcium chloride to produce a calcium phosphate sludge for disposal.

7.2.8 Sludge Generation and Disposal (Question 8a, 8b) (ref. Appendix C, Section 4.0)

The quantities of sludge produced in various areas of the plants and the methods of disposing of the sludge were estimated from the results of Questions 8a and 8b.

The average quantities of sludge collected from rinse tanks, process tanks and treatment plants are shown in Figure 7. The 192 plants which responded to question 8a produced an average of 532 cubic metres/year of sludge from their treatment plants (94 respondents). Much lower quantities of sludge were collected from rinse tanks (17 cubic metres/year)(33 respondents) and from process tanks (10 cubic metres/year)(75 respondents). Small quantities of sludge were also generated from cleaner, settling, or strip tanks, or from painting operations.

The disposal methods employed by the respondents to question 8b are shown in Figure 8. Secure landfill was used by 111 plants. Municipal landfill sites and recycling companies received sludge from 37 and 34 plants respectively. Foundry's accepted sludge from 3 plants. In the other's category, 28 plants hauled sludge off-site but did not indicate the final destination, 7 plants were storing sludge on-site and 6 reused the sludge by selling it to Falconbridge.

7.2.9 Quantities of Metals Purchased

The average quantities of the various metals, metal salts and acids that were purchased by the respondents who use the metal are shown in Table 11. For example, 6 respondents purchased an average of 805 kg/year of chromium oxide for a total of 4,833 kg/year. The six most commonly purchased metals and/or salts are listed below.

Metal/Salt	Millions of Kilograms Per Year	# of Plants
Zinc	42.1	69
Chromic Acid	18.5	91
Aluminum	3.0	9
Nickel	1.7	87
Tin	0.9	33
Copper	0.5	69

The data above represents the total weight of metal and its salts, as extracted from Table 11. For example, 1.7 million pounds of nickel is the sum of the weights for nickel + nickel chloride + nickel sulphate. The weight of aluminum represents the amount purchased for finishing. The data also represents the total number of plants in which one of the metal salts or its metal were used. For example, Table 11 for nickel shows 70 + 50 + 61 = 181 occurrences of nickel or its salts in the question 9 data. This occurred in the 87 plants, as shown above.

Under the "others" title, 74 respondents in Table 11 indicated purchased quantities of other materials, the metal content of which could not be estimated. Various quantities of acids, alkalis and proprietary solutions were also indicated.

7.2.10 Geographic Distribution of Metal Finishing Companies

The locations of the 262 respondents to the survey were summarized by county as shown in Figure 1. The numbers on the map indicate the number of surveyed metal finishing plants that were located in each county. For example, there were 26 metal finishing plants in the County of Waterloo, 1 plant in the County of Thunder Bay, 8 in the County of Ottawa-Carlton and 22 in the County of Peel. The number of plants in each county is also indicated by colour coding. The number of plants in the MOE regions are also shown.

7.2.11 Plant Visits

Part of the survey program was to visit ten plants engaged in metal finishing operations. The plants that were visited were selected based on the type of operations conducted, to cover all the metal finishing operations, a variety of waste treatment methods, the various regions of the Province and the various sizes of the business as described in Section 6.5.

Plants were visited in the following cities: London, St. Catharines, Newmarket, Scarborough, Peterborough, Toronto, Downsview, Mississauga, Thunder Bay and Whitby.

The general results of the plant visits showed that the questionnaire was completed properly and produced a fair overview of the plants' operation. The major conclusions derived from the visits are that:

a) some companies who operated captive shops were actively seeking methods of getting out of the business;
b) most companies were aware of regulations regarding wastewater quality and waste disposal;
c) smaller sized shops used commercial, off-site services to control wastes rather than invest in an in-house pollution control system;
d) several plant managers commented that a loading restriction based on kg of metal pollutant per day rather than a concentration restriction in milligram/litre was required to ensure that all metal finishing companies would treat wastewaters. They believed that too many companies were avoiding the costs of treating wastewaters by diluting them to comply with sewer use by-laws and therefore "legally" obtained a cost advantage in a very competitive business. This survey shows that 52 plants do not treat wastewaters.

7.3 4R's Technology

The reduction in the impact on the environment by wastes from all industries has been addressed by the MOE's 4R's policy. This policy suggests that to reduce impacts industry should apply the principles of reduction, recovery, recycling and reuse. The metal finishing industry has applied these techniques in the manner described below. Some of the discussion presented has already appeared in previous sections of this report.

7.3.1 Reduction

Many operations have been instituted in the metal finishing industry to reduce the quantity of waste produced. One of the major sources of metal or other contamination in rinse waters is dragout. Dragout occurs when parts are transferred from one process bath to the next. Some of the solution, in which the part was immersed, clings to the part and racks or barrels and is transferred to the next bath. This clinging solution is removed in rinse tanks, the water from which, must be treated to remove the contaminants. Any reduction in dragout minimizes the amount of waste that is generated.

The major techniques for minimizing dragout include:

i) longer drain times,
ii) the use of more dilute baths,
iii) careful racking techniques to allow parts to drain properly, and
iv) the reduction of bath viscosity and surface tension using higher temperatures and/or wetting agents.

Each of these techniques is discussed in detail in Appendix C, Section 2.1.

The results of this survey suggest that 53% of the metal finishing companies use at least one of these techniques. One notable reduction technique in chromium electroplating is the use of a trivalent rather than a hexavalent chromium plating bath. The trivalent chrome bath produces a finish over nickel which is corrosion resistant and durable but which is not as shiny as the hexavalent bath's finish. In

many industrial applications where the shiny finish is not required, the trivalent bath, which operates at 20-30 g/L versus 300 g/L for the hexavalent bath, reduces dragout and therefore waste generation by a factor of 8 to 15 times.

A second notable method of reducing waste from alkaline degreasers is the use of ultrafiltration. A carefully designed bath combined with a good ultrafiltration unit can be operated 4 to 10 times longer than the standard bath. The ultrafiltration unit removes oil from the bath plus impurities leaving the caustic behind. Regular makeup of the emulsifying agents etc. maintain the bath's strength thereby extending its useful life.

7.3.2 Recovery

The recovery of valuable chemicals used in the metal finishing industry was not found to be widely practised although many techniques are available. The most common techniques include: i) evaporation, ii) ion exchange, and iii) electrolytic recovery which are described in Appendix C, Section 3.2.

Evaporation and ion exchange are used to make a solution containing high concentrations of metals from dilute rinse waters. The concentrated solutions can then be purified for reuse in the baths directly or, in some cases, the metal is recovered as a metal by electrolytic recovery. The solid metal is then reused as anode material. These recovery techniques are in contrast with the common practice of precipitating the metals as metal hydroxides and disposing of the sludge as a waste.

The results of this survey show that only 20% of the metal finishing companies employ these recovery techniques.

7.3.3 Recycling

The recycling of waste streams within the metal finishing industry is widely used. Among the commonly used recycling techniques were:

i) counter current rinsing
ii) recycle contaminated rinse water
iii) recycle treated effluent

which are described in Appendix C, Sections 2.2 and 2.4.

Counter current rinsing is extremely effective at minimizing the amount of water required to, for example, clean parts between operations i.e. after nickel plating and before chromium solution. The individual rinses are recycled from the successive tanks by transferring the fourth to the third rinse tank, the third to the second and so on.

Counter current rinsing also produces a concentrated solution in the first rinse which is then more economically recycled. One technique is to use the concentrated first rinse to replace evaporative losses from the bath preceding the first rinse.

The evaporation losses are sometimes increased in the process bath by using an air evaporator. This allows more of the first rinse to be recycled to the bath, thereby reducing the amount of rinse water that must treated.

A second recycling system involves the recycling of treated wastewater. Ion exchange is employed to purify rinse waters by removing metallic and ionic impurities including metals and anions such as chlorides or sulphates. The purified water is then recycled back through the rinses water system. Regenerant solutions from the ion exchangers is then processed to recover the metals and possibly acids or treated to precipitate the impurities.

Other recycling scenarios may involve the recycling of water rinses from an acid bath to the rinse water of the alkaline cleaner. This was found in one case to extend the life of the acid bath by reducing the pH of the dragout water to the acidic state from the alkaline bath.

The results of this survey indicate that approximately 79% of the metal finishing companies recycle rinse waters to help minimize waste using at least one of the three scenarios described above.

7.3.4 Reuse

The reuse of waste materials from the metal finishing industry does not appear to be extensive. The results of the survey indicate that most companies treated wastes to produce a metal bearing sludge that was disposed of in either a secure or a municipal landfill. A few had made arrangements with a foundry or Falconbridge to reuse the sludge in the manufacturing of primary metals. It may be possible to encourage more reuse of the metal sludge in this manner. In addition, one firm in the USA will accept sludges bearing as little as 1% of most common metals used in the metal finishing industry. Thirty four plants or 15% of the metal finishing companies sent sludges to the companies which reclaimed the metals.

Spent process solutions can be disposed of through companies who will reclaim the metals or acids for reuse. The use of these companies was indicated in the survey by 53% of the metal finishing companies.

Glossary of Terms

Anion

A term referring to a chemical species dissolved in a solution that has a negative charge i.e. the sulphate anion SO_4^{-2}.

Anode

An electrode in an electroplating or anodizing bath which is positively charged. Metals normally dissolve at the anode.

Anodizing

The conversion of the surface of a metal substrate into an insoluble metal oxide by electrolytic oxidation.

Baume

A term used to indicate the density of a solution i.e. water has a density of 1000 g/L or 0° Baume.

Bright Dipping

A specialized form of etching designed to remove oxide layers on substrates prior to further treatment such as anodizing.

Cathode

An electrode in an electroplating or anodizing bath which is negatively charged. Metals are normally deposited on the cathode.

Cation

A term referring to a metal dissolved in solution that has a positive charge i.e. the nickel cation Ni^{+2}.

Chemical Conversion Coating

The application of a coating to a substrate i.e. phosphating, colouring, passivation and chromating.

Chemical Milling, Etching and Bright Dipping

The removal of small quantities of metals from parts by the controlled dissolution of the metal by chemical agents.

Chromating

The application of a chromium based coating to a substrate to prevent oxidation.

Chromic Oxide

A form of chromium metal (CrO_3) used to make chromic acid when dissolved in sulphuric acid (H_2SO_4).

Colouring

The treatment of a metal surface to produce an acceptable colour.

Current Density

The number of amps of electrical current that can be applied to each m^2 of surface of the part being plated or anodized. It is measured in amperes per square metre symbolized by A/m^2.

Cyanide Bath

A term referring to a metal finishing bath that contains cyanide anions (CN^-). Cyanide was used extensively in electroplating baths because it produced a good, even deposit and it was not sensitive to impurities. Its use has been greatly reduce due to the need for pollution control.

Electrodeposition

The deposition of a metal onto a substrate by the application of an electric current.

Electroless Plating

The chemical reduction process which catalytically deposits a metal ion from solution onto a substrate without the use of external electrical energy.

Electroplating

The deposition of a thin layer of a metal from solution onto a substrate by the application of an electric current (electrodeposition).

Electropolishing

An electrolytic process which removes metal from the surface of the substrate to create a very smooth surface for decorative reasons.

Etching

The removal of a small amount of metal from the substrate to attain specific design configurations and tolerances of surface appearance.

Hexavalent Chromium

A term referring to the chromium anion with 6 positive charges (Cr^{+6}).

Hot Dipping

The deposition of a metal on a substrate by immersing the part in molten metal.

Immersion Plating

The deposition of a thin layer of metal from solution onto a substrate by the chemical displacement of the base metal.

Milling

The same as etching except larger quantities of metals are removed.

Passivation

The treatment of a substrate to improve corrosion resistance (for example passifying stainless steel using nitric acid).

Phosphating

The treatment of a metal surface to produce a coating of insoluble metal phosphate crystals which strongly adhere to the substrate.

Plant or Company

A location where metal finishing operations are conducted i.e. some companies have several plants.

Stripping

The removal of a metal finish from the substrate using immersion or electrolytic methods.

Sulphuric Acid

An acid with the chemical formula H_2SO_4.

Throwing Power

A term referring to the ability of an electroplating bath to deposit the metal evenly over the surface of the part being plated. For example, a high throw bath deposits metal evenly over parts with an irregular shape, whereas a bath with low throwing power does not.

Trivalent Chromium

A term referring to the chromium anion with 3 positive charge (Cr^{+3}).

Units

1 m^3	=	35.315 ft^3
1 oz/gal	=	7.49 g/L
1 Kg	=	2.2 lb

TABLE 1 - TYPES OF METAL FINISHING OPERATIONS

TYPE OF ACTIVITY	# PLANTS INVOLVED	# PLANTS DEDICATED
METAL FINISHING	262	NA
ELECTROPLATING	168	34
ANODIZING	38	2
CHEMICAL CONVERSION COATING	158	42
ELECTROLESS PLATING	49	0
CHEMICAL ETCHING AND MILLING OR BRIGHT DIPPING	121	9
PRINTED CIRCUIT BOARD MANUFACTURING	21	NA
HOT DIP COATING	26	7
		104

TABLE 2 - DISTRIBUTION OF DOLLAR SPENT IN PURCHASING METALS OR METAL SALT

$ SPENT	# PLANTS	%	CUM %
0*	12	5.91	5.91
0 < $ < = 1 K	13	6.40	12.32
1 K < $ < = 5 K	28	13.79	26.11
5 K < $ < = 10 K	15	7.39	33.50
10 K < $ < = 50 K	49	24.14	57.64
50 K < $ < = 100 K	26	12.81	70.44
100 K < $ < = 500 K	32	15.76	86.21
500 K < $ < = 1 M	9	4.43	90.64
1 M < $ < = 5 M	12	5.91	96.55
5 M < $ < = 10 M	2	0.99	97.54
> 10 M	5	2.46	100.00
TOTAL	203	100.00	

Notes:
1. See also Figure 2.

0* No metals or metal salts purchased.
But other metal finishing solutions such as acids may have been purchased.

TABLE 3 - DETAILED FEATURES OF ELECTROPLATING PLANTS

METAL	NUMBER OF PLANTS						
	ENGAGED	HANDLING METHOD USED				TREATING RINSE WATER	NOT TREATING RINSE WATER
		R	C	B	O		
TOTAL NUMBER OF PLANTS	168						
BRASS	22	15	0	8	2	21	1
BRONZE	5	4	0	1	1	5	0
COPPER NON-CYANIDE	41	35	2	1	3	29	12
COPPER - CYANIDE	44	31	0	18	2	37	7
CADMIUM NON-CYANIDE	2	1	0	0	1	2	0
CADMIUM CYANIDE	16	11	0	9	0	10	6
ALUMINUM	9	4	4	1	0	5	4
IRON	3	1	1	0	1	1	2
LEAD	3	1	0	0	2	2	1
LEAD-TIN	19	17	1	2	1	14	5
NICKEL - WATTS	62	46	5	12	4	46	16
NICKEL - SULFAMATE	31	24	0	7	2	20	11
CHROMIUM	65	55	3	2	5	52	13
TIN - ALKALINE STANNATE	10	3	2	2	4	8	2
TIN - STANNOUS FLUOBORATE	3	2	0	1	0	2	1
TIN - STANNOUS SULFATE	17	12	2	9	0	12	5
TIN ALLOY - COPPER	5	3	0	2	0	3	2
TIN ALLOY - ZINC	5	2	0	4	0	3	2
TIN ALLOY - NICKEL	12	7	1	2	2	10	2
ZINC CYANIDE	12	5	0	9	0	10	2
ZINC NON-CYANIDE	36	16	2	22	3	28	8
GOLD CYANIDE	20	14	2	3	3	14	6
GOLD NON-CYANIDE	12	9	2	1	0	6	6
SILVER	24	16	2	8	3	19	5
RHODIUM	8	7	0	0	1	6	2
PALLADIUM CYANIDE	1	0	0	0	1	1	0
PALLDIUM NON-CYANIDE	2	0	1	0	1	1	1
PLATINUM	2	0	1	0	1	1	1
INDIUM	1	0	0	0	1	1	0
RUTHENIUM	1	0	0	0	1	1	0
IRIDIUM	0	0	0	0	0	0	0
OSMIUM	0	0	0	0	0	0	0
TOTAL NUMBER OF OPERATIONS	493	341	31	124	45	370	123

NOTES:
R - RACK
C - COIL
B - BARREL
O - OTHERS

TABLE 4 - DETAILED FEATURES OF ELECTROLESS PLATING PLANTS

METAL	NUMBER OF PLANTS						
	ENGAGED	HANDLING METHOD USE				TREATING	NOT TREATING
		R	C	B	O	RINSE WATER	RINSE WATER
TOTAL NUMBER OF PLANTS	49						
NICKEL	18	15	2	5	1	13	5
COPPER	24	22	2	0	0	15	9
GOLD	2	2	0	0	0	1	1
IRON	0	0	0	0	0	0	0
PALLADIUM	4	4	0	1	0	3	1
ARSENIC	1	0	0	0	1	0	1
CHROMIUM ACID	2	1	0	1	0	1	1
CHROMIUM ALKALINE	0	0	0	0	0	0	0
SILVER	4	3	0	1	0	3	1
BRASS	0	0	0	0	0	0	0
BRONZE	0	0	0	0	0	0	0
TIN	2	2	0	0	0	1	1
OTHERS:							
NICKEL SULFATE	1	0	0	0	0	1	0
TITAMIUM	1	0	0	0	0	1	0
TOTAL NUMBER OF OPERATIONS	59	49	4	8	2	39	20

NOTES:
R - RACK
C - COIL
B - BARREL
O - OTHERS

TABLE 5 - DETAILED FEATURES OF CHROMATING PLANTS

TYPE	# PLANTS						
	ENGAGED	PARTS HANDLING METHOD				TREATING RINSE WATER	NOT TREATING RINSE WATER
		R	C	B	O		
Total Number of Plants	58						
Black Oxidizing	16	9	2	6	1	11	5
Sealing Rinses	38	22	2	16	1	29	9
Cyanide Bearing	4	2	0	0	2	2	2
Total Number of Operations	116	33	4	22	4	42	16

NOTE:
R - Rack
C - Coil
B - Barrel
O - Others

TABLE 6 - DETAILED FEATURES OF HOT DIPPING PLANTS

TYPE	# PLANTS						
	ENGAGED	PARTS HANDLING METHOD				TREATING RINSE WATER	NOT TREATING RINSE WATER
		R	C	B	O		
Total Number of Plants	26						
Zinc	10	4	3	2	1	8	2
Tin	10	6	2	0	2	4	6
Lead	6	3	1	0	2	2	4
Aluminum	2	0	1	0	1	1	1
Total Number of Operations	28	13	7	2	6	15	13

NOTE:
R - Rack
C - Coil
B - Barrel
O - Others

TABLE 7 - DETAILED FEATURES OF ANODIZING PLANTS

TYPE	# PLANTS						
	ENGAGED	PARTS HANDLING METHOD				TREATING	NOT TREATING
		R	C	B	O	RINSE WATER	RINSE WATER
Total Number of Plants	38						
Aluminum	30	27	3	0	0	21	9
Magnesium	1	1	0	0	0	1	0
Zinc	2	1	0	1	0	2	0
Titanium	0	0	0	0	0	0	0
Total Number of Operations	33	29	3	1	0	24	9

NOTE:
R - Rack
C - Coil
B - Barrel
O - Others

TABLE 8 - DETAILED FEATURES ON CHEMICAL MILLING, ETCHING, BRIGHT DIPPING, STRIPPING AND ELECTROPOLISHING PLANTS

ACTIVITY	# PLANTS						
	METAL OR BATH	ENGAGED	PARTS HANDLING METHOD				TREATING
			R	C	B	O	RINSE WATER
Milling & Etching	Overall	62					
	Ferric Chloride Bath	11	10	1	0	0	6
	Ammonium Persulfate	7	6	1	0	0	3
	Cupric Chloride	2	0	0	0	2	1
	Chromic	8	6	1	1	0	6
	Sodium Hydroxide	28	19	4	4	0	22
	Others	28	0	0	0	0	0
Bright Dipping of	Overall	43					
	Copper	26	16	1	10	1	18
	Aluminum	14	12	0	2	0	11
	Nickel	4	3	1	0	0	3
	Zinc	3	1	0	2	0	3
	Cadmium	1	1	0	0	0	1
	Silver	2	2	0	1	0	2
	Others	9	0	0	0	0	0
Stripping		47	38	2	8	2	37
Electropolishing		9	5	1	3	0	6

NOTE:
R - Rack
C - Coil
B - Barrel
O - Others

TABLE 9 - WATER REDUCTION MEASURES AND PRACTICES

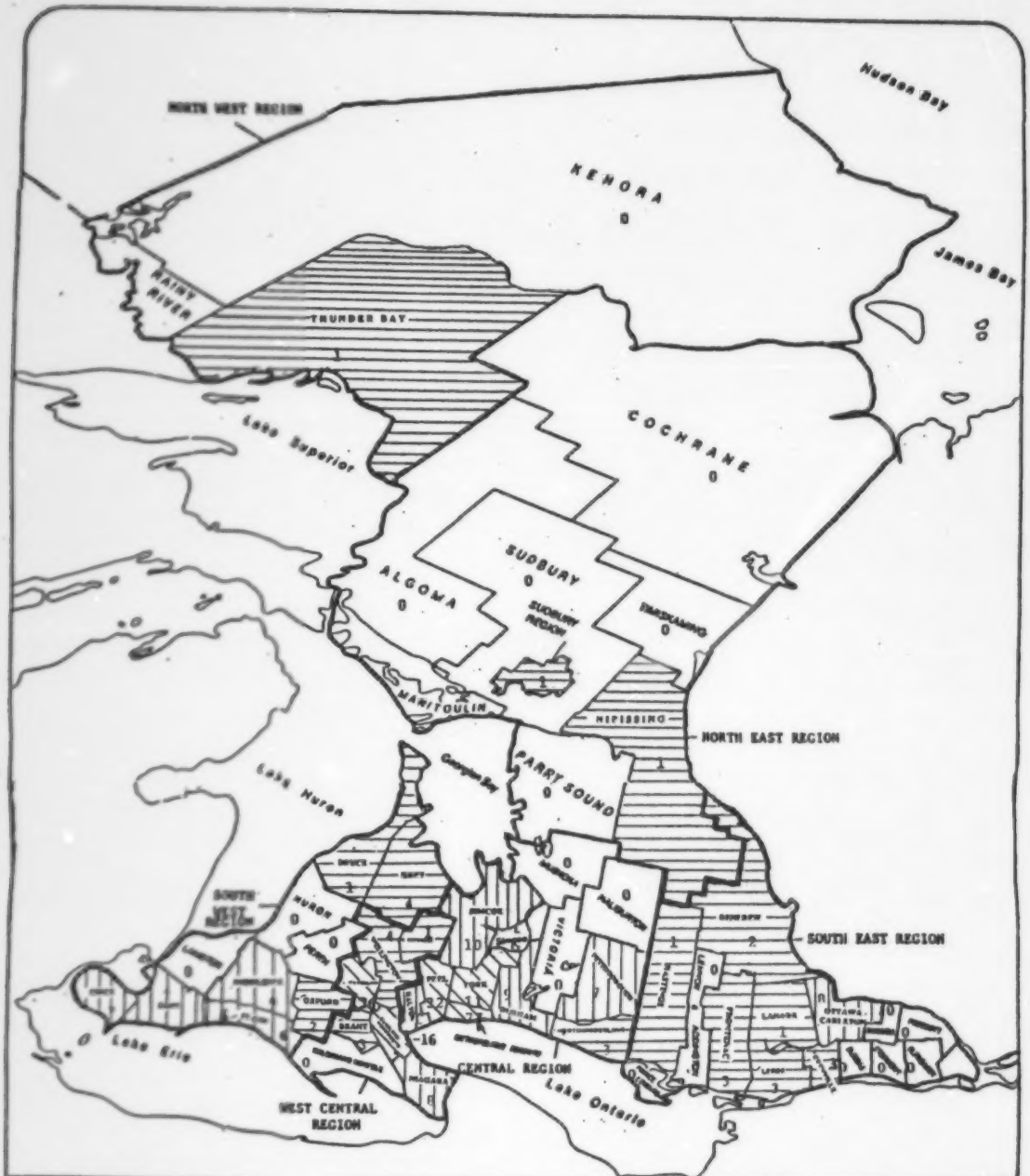
METHODS	NUMBER OF PLANTS		
	YES	PLANNED	NO
Overall	199	17	37
Counterflow Rinsing	120	2	
Spray Rinsing	93	0	
Conductivity Cells	22	0	
Flow Restrictors in Rinse Tanks	76	3	
Dragout Minimization by:			
Longer Withdrawal/Drainage Time	98	2	
Use of Wetting Agent	41	1	
Reusing Contaminated Rinse Water and Treated Effluent	70	8	
Others	37		

TABLE 10 - RINSE WATER TREATMENT METHODS

METHOD	NUMBER OF PLANTS		
	YES	PLANNED	NO
Overall	184	15	52
Neutralization	141	6	
Cyanide Destruction	45	1	
Precipitation	88	2	
Gravity Settling	105	3	
Filtration	91	3	
Chlorination	29	0	
Hexavalent Chromium Reduction	75	0	
Evaporation	24	1	
Ion Exchange	10	0	
Electrolytic Recovery/Destruction	18	0	
Ultrafiltration	2	2	
Others	26		

TABLE 11 - METAL AND METAL SALT PURCHASES

CHEMICAL	OCCURRENCES	AVERAGE KG/YEAR	TOTAL KG/YEAR
Chromium Oxide	6	805	4,833
Chromic Acid	86	214,787	18,471,666
Nickel	70	20,641	1,444,895
Nickel Chloride	50	1,596	79,795
Nickel Sulfate	61	3,404	207,622
Copper	50	6,929	346,432
Copper Sulfate	39	2,628	102.499
Copper Chloride	4	447	1,787
Copper Fluoborate	1	409	409
Copper Pyrophosphate	1	0	0
Copper Cyanide	42	301	12,657
Copper Nitrate	0	0	0
Cadmium Oxide	9	289	2,598
Cadmium Fluoborate	0	0	0
Brass	15	590	8,850
Bronze	3	1,031	3,093
Aluminum	9	334,970	3,014,726
Iron	1	227	227
Ferrous Sulfate	7	2,726	19,081
Ferric Chloride	11	16,255	178,805
Lead	10	5,656	56,564
Lead Fluoborate	14	151	2,119
Zinc	54	780,498	42,146,902
Zinc Cyanide	15	173	2,598
Tin	23	40,421	929,681
Tin Fluoborate	16	448	7,164
Gold	22	75	1,650
Silver	21	113	2,367
Platinum	0	0	0
Palladium	3	25	76
Rhodium	5	0	2
Indiumium	0	0	0
Ruthenium	0	0	0
Iridium	0	0	0
Osmiun	1	23	23
Others	74		



METAL FINISHING SURVEY EO 88179
FIGURE 1
GEOGRAPHICAL DISTRIBUTION OF SURVEYED METAL FINISHING PLANTS IN ONTARIO

Proctor & Redfern Limited
Consulting Engineers and Architects
Toronto

Legends:

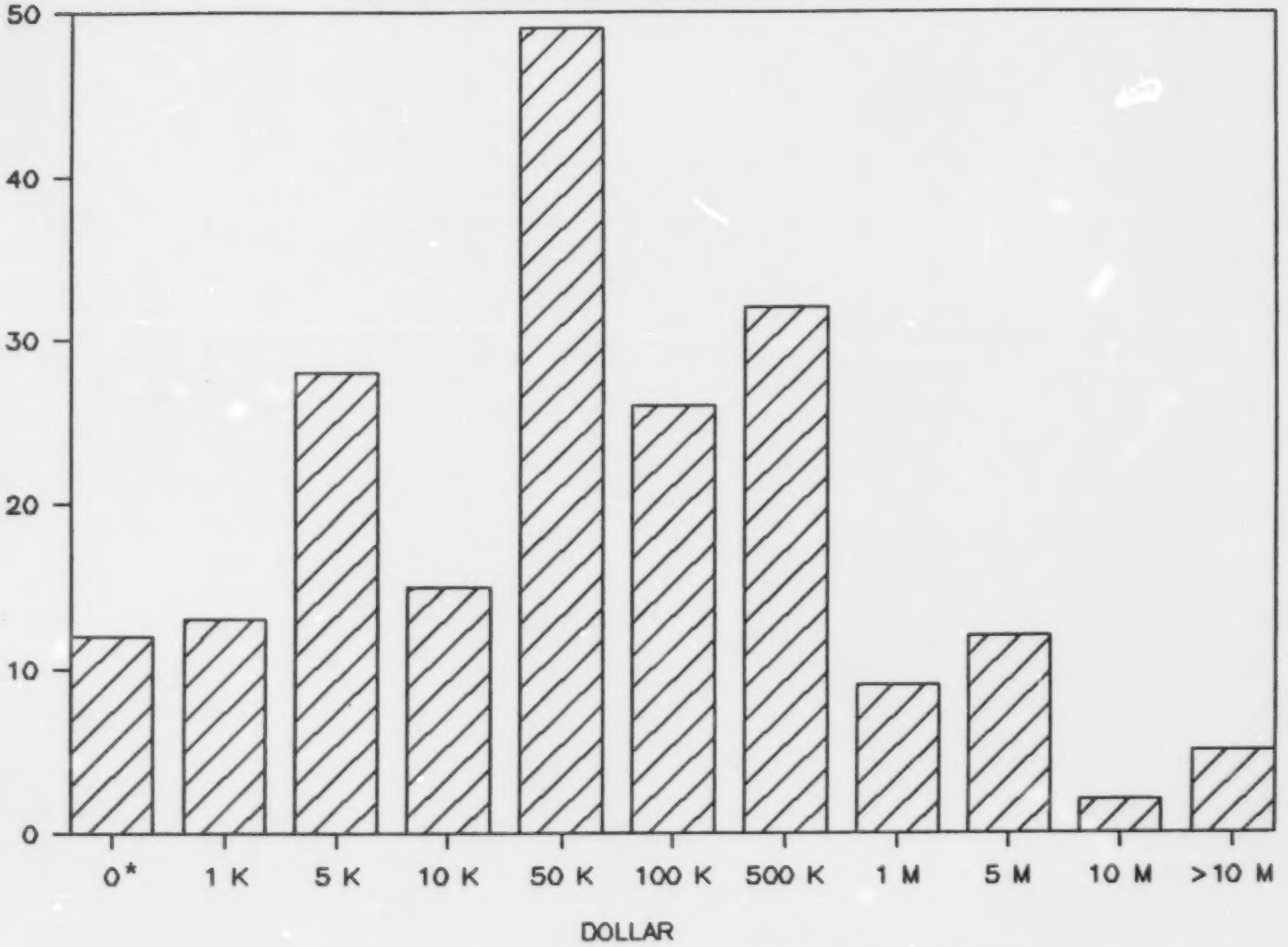
0	Plant	
1 - 4	Plants	
5 - 10	Plants	
> 10	Plants	
MOE Region Border		

Table of Totals by MOE Regions:

MOE Region	# of Plants
South West	36
West Central	58
Central	147
South East	18
North East	2
North West	1

METAL FINISHING SURVEY

FIG 2: DOLLAR SPENT ON METALS & SALTS

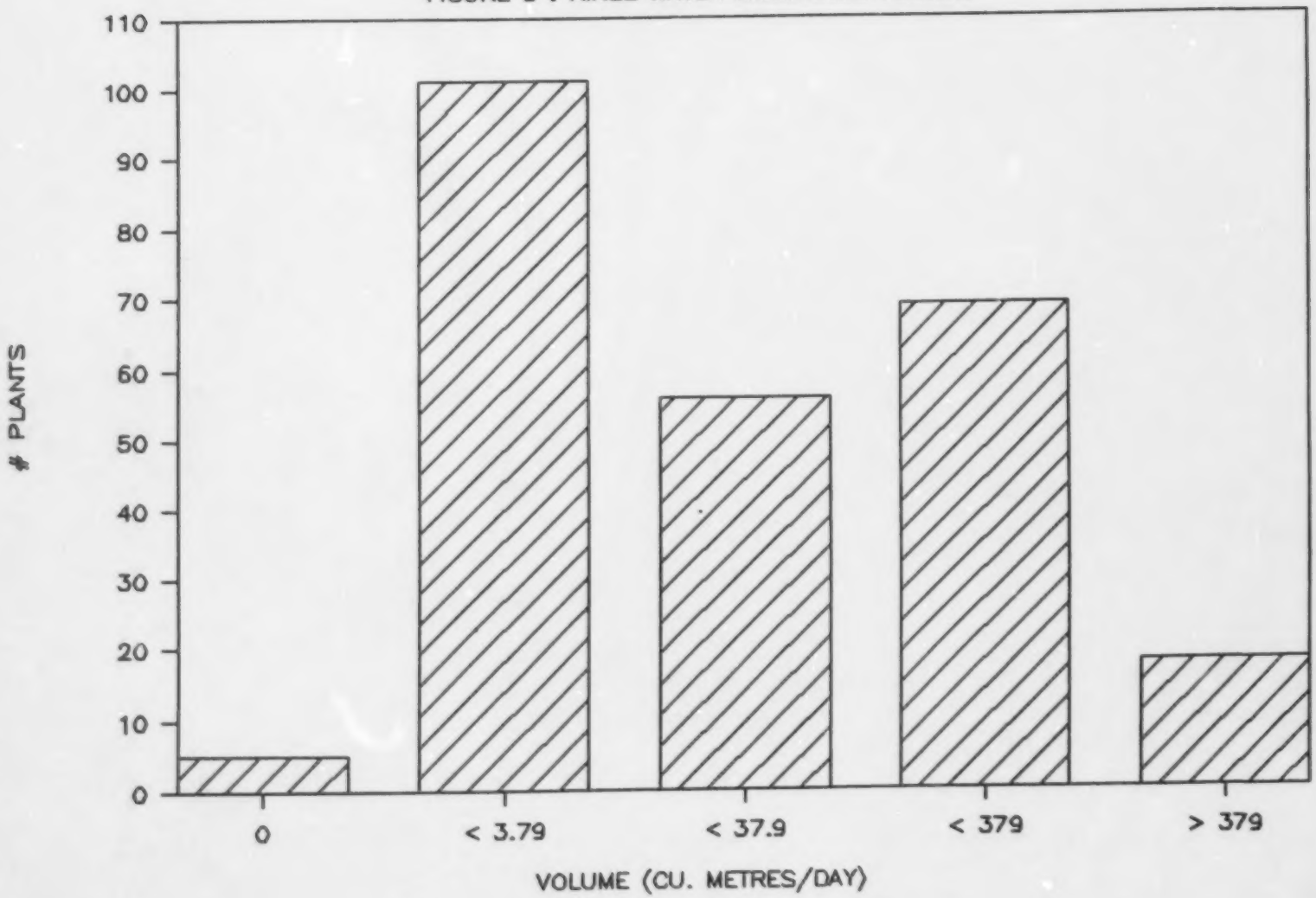


0* No metal or metal salts purchased. But other metal finishing solutions such as acids may have been purchased.

Total Number of Respondents = 203

METAL FINISHING SURVEY

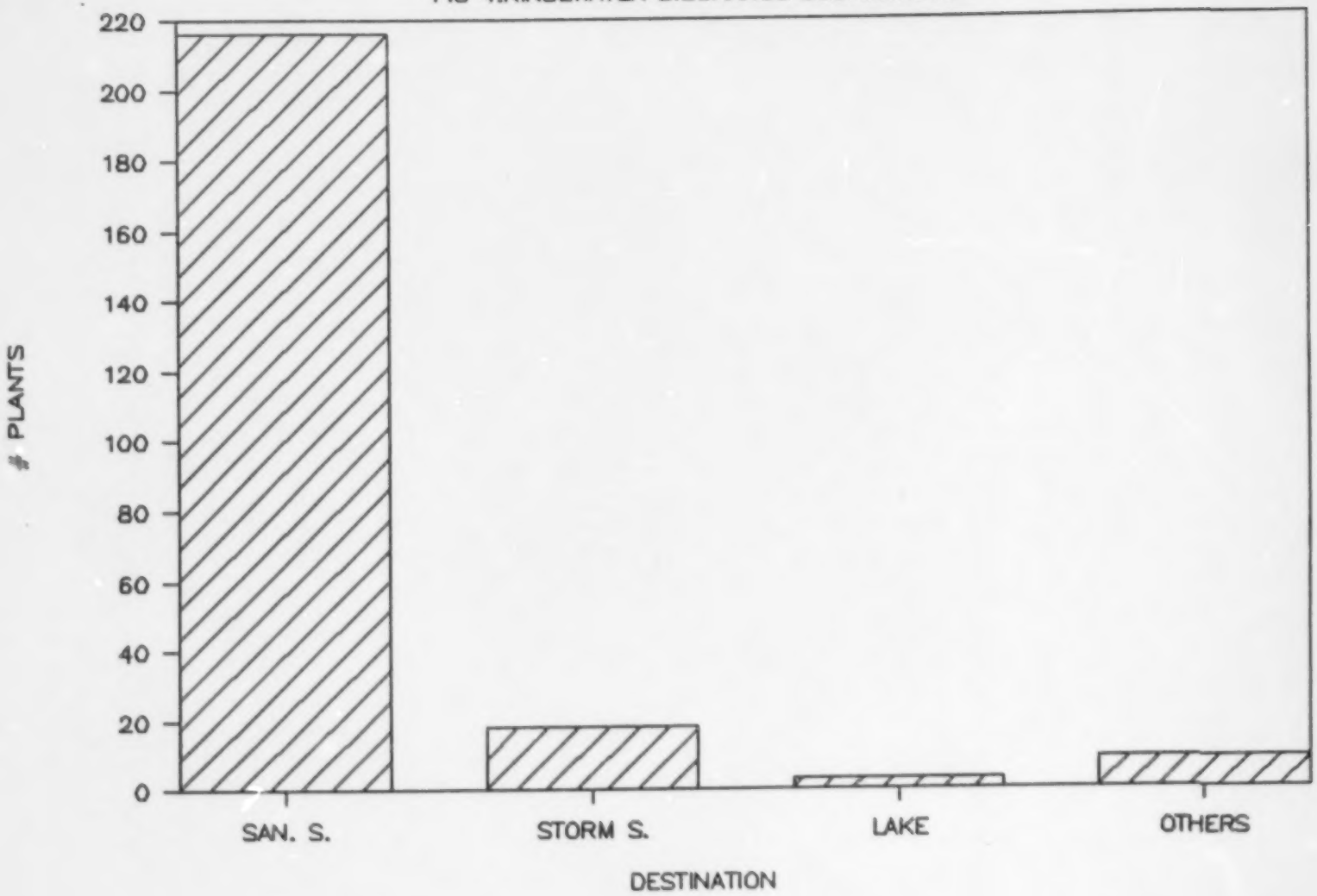
FIGURE 3 : RINSE WATER DISCHARGE VOLUME



Total Number of Respondents = 249

METAL FINISHING SURVEY

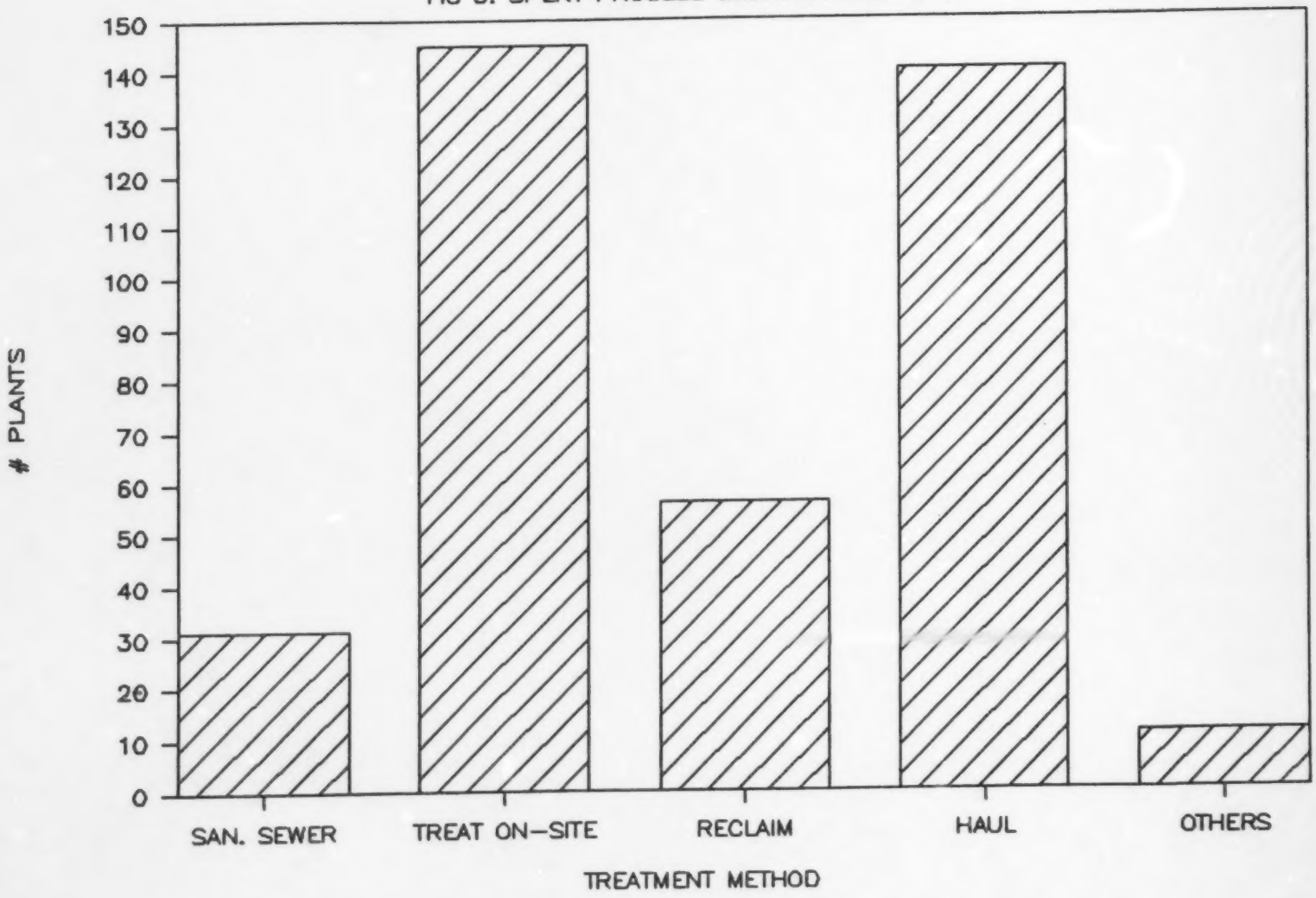
FIG 4:RINSEWATER DISCHARGE DESTINATIONS



Total Number of Respondents = 244

METAL FINISHING SURVEY

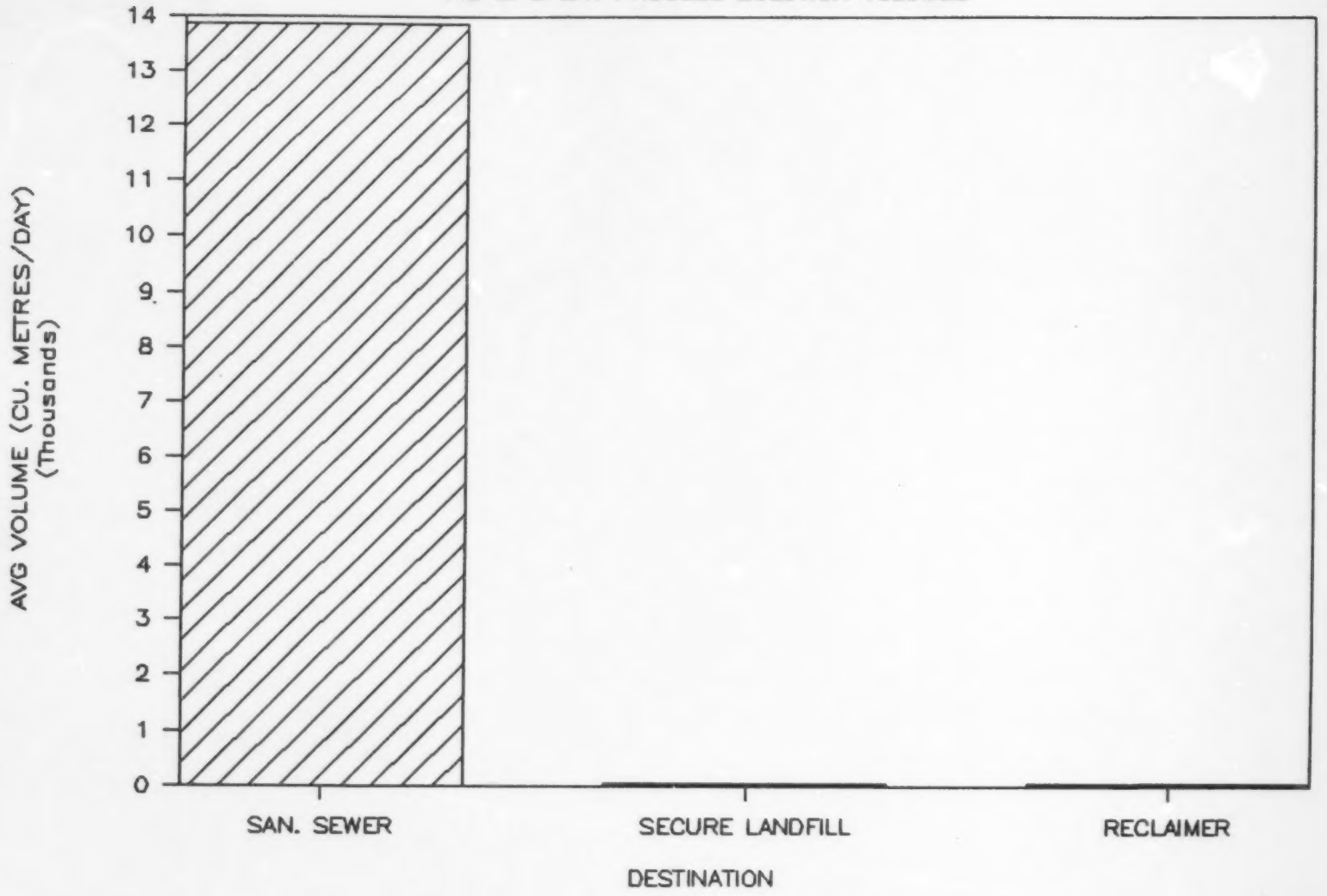
FIG 5: SPENT PROCESS SOLUTION TREATMENT



Total Number of Respondents = 244

METAL FINISHING SURVEY

FIG 6: SPENT PROCESS SOLUTION VOLUMES

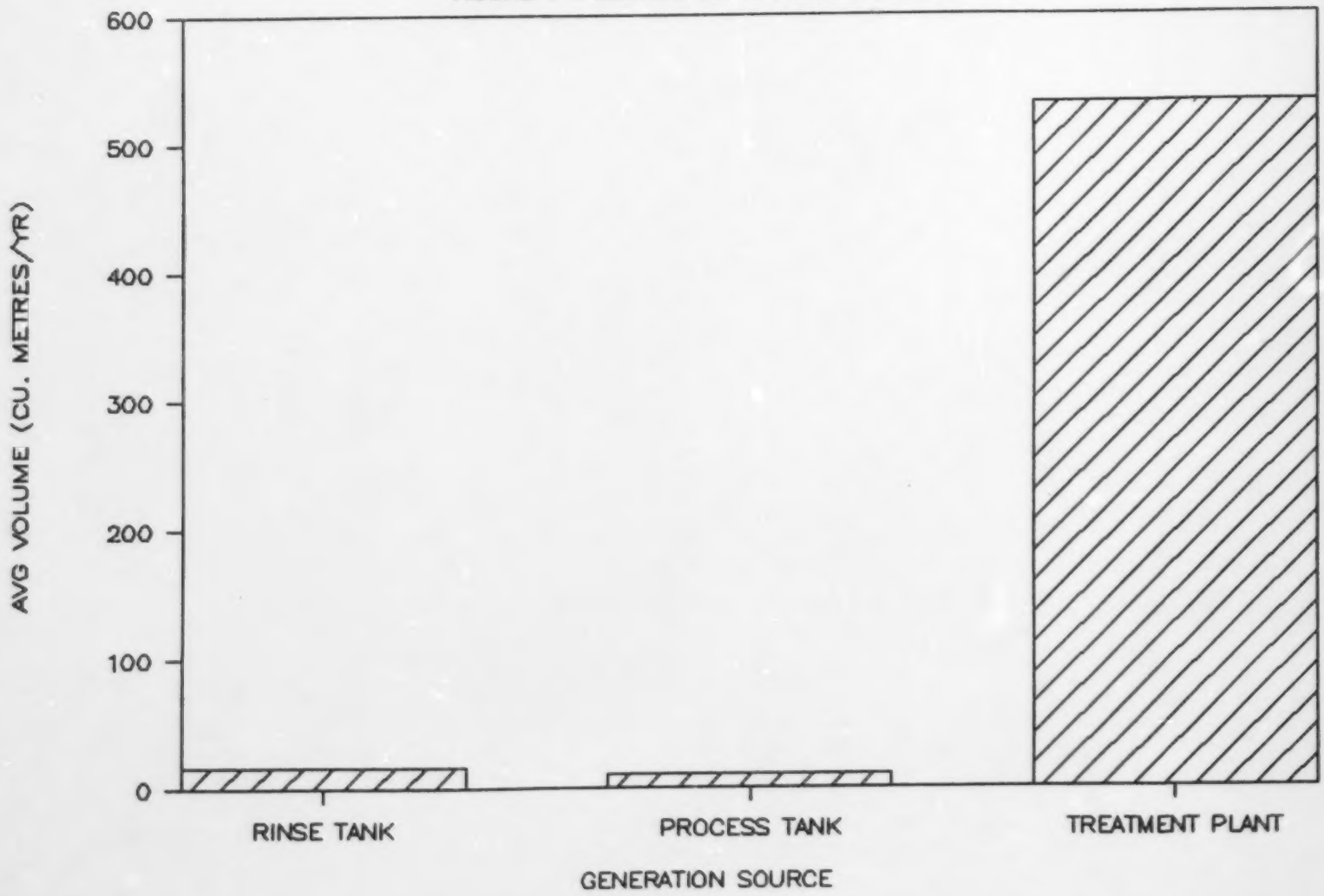


	SAN. SEWER	SECURE LANDFILL	RECLAIMER
# Respondents	120	46	63

Total Number of Respondents = 207

METAL FINISHING SURVEY

FIGURE 7 : SLUDGE GENERATION VOLUMES

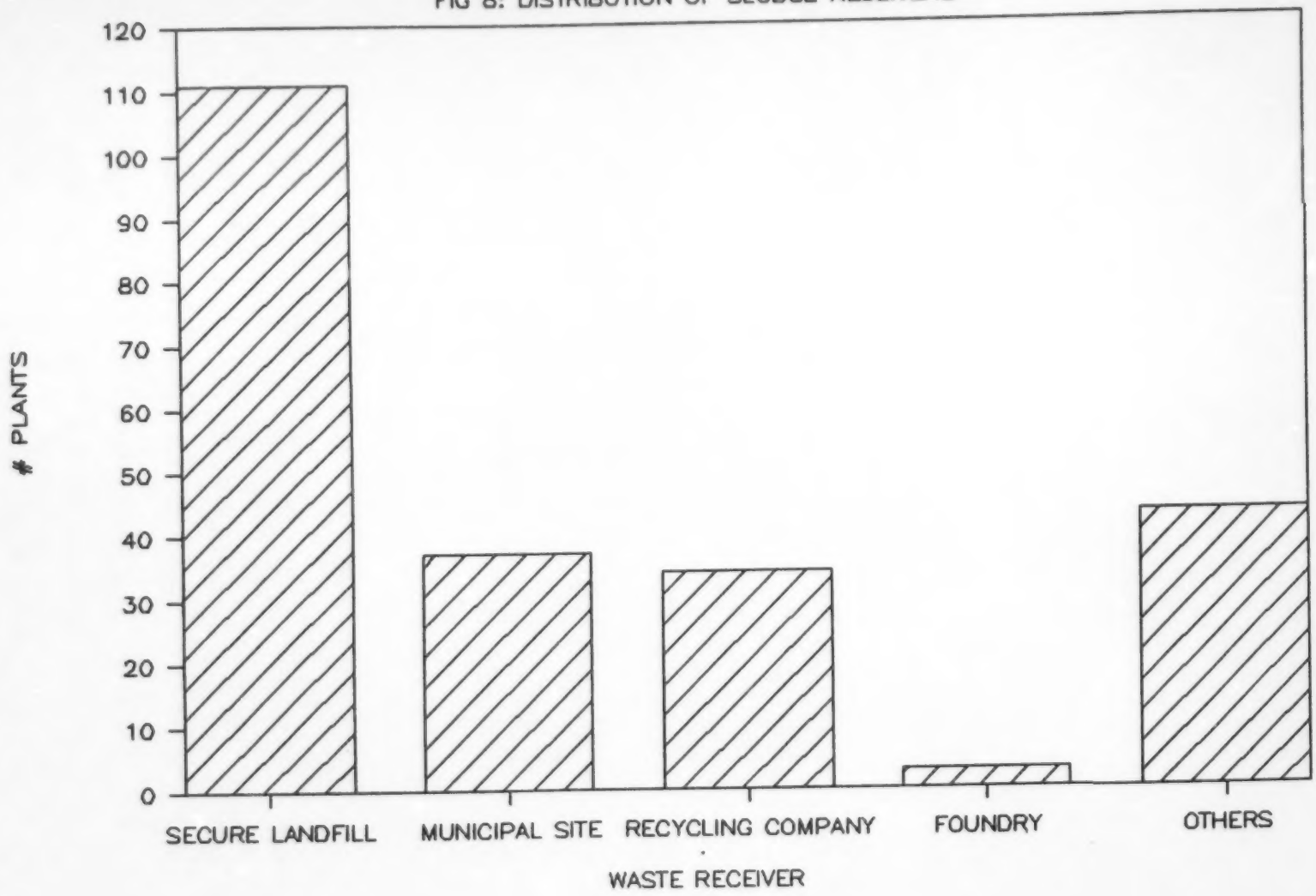


# Respondents	33	75	94

Total Number of Respondents = 192

METAL FINISHING SURVEY

FIG 8: DISTRIBUTION OF SLUDGE RECEIVERS



Total Number of Respondents = 195

APPENDIX A

THE QUESTIONNAIRE

METAL FINISHING SURVEY

Company Name:

Address:

Telephone:

GRR Number (if applicable):

Questionnaire completed by:

Title/position: Date:

1. Are you engaged in any of the following Metal Finishing activities?

Common and precious metal electroplating	:	Yes / No
Anodizing	:	Yes / No
Chemical conversion coatings (e.g. coloring, phosphating, passivation, chromating, and immersion plating)	:	Yes / No
Electroless plating	:	Yes / No
Chemical etching and milling or bright dipping	:	Yes / No
Printed circuit board manufacturing	:	Yes / No
Hot Dip Coating (e.g. galvanizing)	:	Yes / No

If you answered "Yes" for one or more questions, please proceed to fill out the questionnaire.

If you answered "No" to all the questions, please complete the information on company name, address etc. and return only page 1 of the questionnaire to Proctor & Redfern Limited, 45 Green Belt Drive, Don Mills, Ontario, M3C 3K3 to the attention of Dennis Anderson.

If you have any questions regarding the survey, please contact Dennis Anderson at Proctor & Redfern Limited (416-445-3600).

2. How much money do you spent each year buying metals and metal salts for your metal finishing operations? $_____

3. Please put an appropriate mark in the boxes opposite each metal finishing operation to answer the following questions.

column (I) Do you perform this metal finishing operation?
Check (✓) if the answer is "Yes", leave blank if the answer is "No".

column (II) Do you handle the parts being finished in barrels, on racks or as coils (i.e. wire, strip stock etc.)?
Indicate B for barrels
R for racks
C for coils

column (III) Do you treat the rinse waters from this operation prior to discharging to the sanitary sewer, storm sewer etc.?
Check (✓) if the answer is "Yes", leave blank if the answer is "No".

Example: If you plate chromium onto parts held in barrels and treat the rinse waters your response would be as shown below:

	I	II	III
Chromium	✓	B	✓

3a) Electroplating: the deposition of a thin layer of a metal from solution onto a substrate by electrodeposition.

		I	II	III
Brass				
Bronze				
Copper	non-cyanide			
	cyanide			
Cadmium	non-cyanide			
	cyanide			
Aluminum				
Iron				
Lead				
Lead-Tin				
Nickel	Watts			
	sulfamate			
Chromium				
Tin	alkaline stannate			
	stannous fluoborate			
	stannous sulfate			

		I	II	III
Tin Alloys	Copper			
	Zinc			
	Nickel			
Zinc	cyanide			
	non-cyanide			
Gold	cyanide			
	non-cyanide			
Silver				
Rhodium				
Palladium	cyanide			
	non-cyanide			
Platinum				
Indium				
Ruthenium				
Iridium				
Osmium				

Others (specify) _____

3b) Electroless Plating: the chemical reduction process which catalytically deposits a metal ion from solution onto a substrate without the use of external electrical energy.

		I	II	III
Nickel				
Copper				
Gold				
Iron				
Palladium				
Arsenic				
Chromium	acid			
	alkaline			
Silver				
Brass				
Bronze				
Tin				

Others (specify) _____

3c)Immersion Plating: the deposition of a thin layer of metal from solution onto a substrate by chemical displacement of the base metal.

Please specify the metal deposited and the substrate. For example, copper on aluminum, nickel on steel etc.

	I	II	III
_____	__	__	__
_____	__	__	__
_____	__	__	__

3d)Chemical Conversion Coating: the application of a coating to a substrate.

	I	II	III
Phosphating	__	__	__

Please specify _____

	I	II	III
Colouring	__	__	__

Please specify _____

	I	II	III
Passivation	__	__	__

Please specify _____

		I	II	III
Chromating	black oxidizing	__	__	__
	sealing rinses	__	__	__
	cyanide bearing	__	__	__

Please specify _____

3e)Hot Dipping: the deposition of a metal on a substrate by immersing the part in molten metal.

			I	II	III
Hot dipping	zinc	(galvanizing)	__	__	__
	tin		__	__	__
	lead		__	__	__
	aluminum		__	__	__

Flux is flux used? Yes / No

3f) **Anodizing:** the conversion of the surface of a metal substrate into an insoluble metal oxide by electrolytic oxidation.

		I	II	III
Anodizing	aluminum	☐	☐	☐
	magnesium	☐	☐	☐
	zinc	☐	☐	☐
	titanium	☐	☐	☐

3g) **Chemical Milling, Etching and Bright Dipping:** the removal of small quantities of metals from parts by the controlled dissolution of metal by chemical agents.

		I	II	III
Milling & Etching	ferric chloride bath	☐	☐	☐
	ammonium persulfate	☐	☐	☐
	cupric chloride	☐	☐	☐
	chromic	☐	☐	☐
	sodium hydroxide	☐	☐	☐

Others (specify)_____

		I	II	III
Bright Dipping of	copper	☐	☐	☐
	aluminum	☐	☐	☐
	nickel	☐	☐	☐
	zinc	☐	☐	☐
	cadmium	☐	☐	☐
	silver	☐	☐	☐

Others (specify) _____

	I	II	III
Stripping	☐	☐	☐

Please specify _____

	I	II	III
Electropolishing	☐	☐	☐

Please specify _____

Others (specify) _____

4.Have you taken steps to reduce water consumption?

Yes___ No___ Planned___

If answered "Yes", please indicate method:

- Counterflow rinsing |___|
- Spray rinsing |___|
- Conductivity cells |___|
- flow restrictors in rinse tanks |___|
- Drag-out minimization by:
  - longer withdrawal/drainage times |___|
  - use of wetting agents |___|
- Reusing contaminated rinse water and treated effluent |___|
- Others (specify):_____

5.Do you treat your rinse waters?

Yes___ No___ Planned___

If answered "Yes", please indicate all applicable methods:

- Neutralization |___|
- Cyanide destruction |___|
- Precipitation |___|
- Gravity settling |___|
- Filtration |___|
- Chlorination |___|
- Hexavalent chromium reduction |___|
- Evaporation |___|
- Ion exchange |___|
- Electrolytic recovery/destruction |___|
- Reverse osmosis/ultrafiltration |___|
- Others (specify):_____

6.a)What is the approximate volume of wastewater discharged off-site from your metal finishing operations?

Less than 1,000 US gal/day |___|
From 1,000 to 10,000 US gal/day |___|
From 10,000 to 100,000 US gal/day |___|
Others (specify) _____

6.b)What is the ultimate destination of the wastewater discharged?

Municipal sanitary system |___|
Storm sewer |___|
Direct discharge to a lake or stream |___|
Others (specify):_____

7.a)What do you do with spent process solutions?
(indicate all applicable methods)

Discharge directly to municipal sanitary sewer	☐
Treat on-site	☐
Reclaim materials or chemicals	☐
Haul off-site	☐

Others (specify):_____

7.b)If you treat, reclaim or regenerate spent process solutions on-site, please indicate treatment method(s) used:

7.c)Approximate the total quantity of spent process solutions, treated or untreated, that are:

i) Discharged into the sanitary sewer _____ US gal/year
ii) Sent to secure landfill _____ US gal/year
iii) Sent to reclaimer _____ US gal/year
iv) Others (specify) _____

8.a)How much sludge is generated from your metal finishing operations?

Total from rinse tank(s)	_____ ft^3/year
Total from process tank(s)	_____ ft^3/year
Total from treatment plant(s)	_____ ft^3/year

Others (specify) _____

b)Who receives sludges from your plant?

Secure landfill site	Yes / No
Municipal landfill site	Yes / No
Metal recycling company	Yes / No
Foundry	Yes / No

Others (specify):_____

9. How many pounds of the various metal(s) or metal salts do you buy in one year for your metal finishing baths?

Metal	lbs/year	Metal	lbs/year
Chromium Oxide		Ferrous Sulfate	
Chromic Acid		Ferric Chloride	
Nickel		Lead	
Nickel Chloride		Lead Fluoborate	
Nickel Sulfate		Zinc	
Copper		Zinc Cyanide	
Copper Sulfate		Tin	
Copper Chloride		Tin Fluoborate	
Copper Fluoborate		Gold	
Copper Pyrophosphate		Silver	
Copper Cyanide		Platinum	
Copper Nitrate		Palladium	
Cadmium Oxide		Rhodium	
Cadmium Fluoborate		Indium	
Brass		Ruthenium	
Bronze		Iridium	
Aluminum		Osmium	
Iron			
Others (specify) _____			

10. Describe briefly (in 150 words or less) the manufacturing operations at your plant especially as they pertain to metal finishing activities, if you have time.

_____

_____

_____

_____

_____

_____

_____

_____

APPENDIX B

DESCRIPTION OF METAL FINISHING PROCESSES

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1.0 INTRODUCTION

Metal finishing is a rather flexible term which can denote any one of a large number of diverse operations. For the purposes of this project, a Metal Finishing plant was restricted to a facility engaged in one or more of the following activities: electroplating of common and precious metals, electroless plating, anodizing, chemical conversion coating (i.e. phosplating, chromating, and colouring), chemical milling and etching, and printed circuit board manufacturing. However, the scope was also extended to include plants involved in hot dipping since this is carried out at a large number of Ontario metal finishing companies.

Metal finishing plants may be divided into two broad sectors, namely captive shops and job shops. Jobs shops are those that are engaged primarily in doing work for others on a contract basis. Captive facilities are those that perform work chiefly as part of a larger operation. For example, integrated steel complexes conduct a variety of metal finishing operation as do large automotive, appliance, electronics, die casting, etc. companies.

Metal finishing operations very greatly in size, age, number of employees, and number and type of operations carried out. Most small jobs have less than 10 employees, while large job or captive facilities may employ hundreds of production workers. Some plants specialize in only a few activities, while others may perform a lot of metal finishing operations. Surface area of products involved per day can vary from 10 m^2 to more than 1000 m^2. On a weight basis, products processed can range from less than 30 grams to more than 10 tons. Some plants operate only 8 hours/day; however, certain items e.g. wire and strip are processed continuously.

The chief base materials (or workpieces) in the metal finishing industry are usually metals, ranging from common metals to expensive alloys and precious metals. However, at some sites, the predominant base materials are plastics, ceramics or glass.

Solutions used in the metal finishing unit operations contain acids, bases, cyanide, metals, complexing agents, organic additives, oils, detergents and other sundry chemicals, all of which may enter the waste streams during the production steps.

The amount of published information on metal finishing processes is enormous. In addition to standard textbooks, guides and pamphlets published by various technical/trade associations, and literature from suppliers, a number of industry journals such as "Plating and Surface Finishing", "Metal Finishing", "Products Finishing", etc., frequently carry articles on various aspects of metal finishing.

The descriptive summaries appearing in the ensuing sections were abstracted from a list of sources; however, only the seven major references consulted are listed at the end under the heading "General Bibliography".

2.0 ELECTROPLATING

In the electroplating process a metal coating for decorative or functional purposes is applied upon another metal by electrodeposition. Thickness of the deposit can vary; generally speaking, decorative coatings are thin, while much thicker coating are produced for functional, or engineering applications.

The objects to be plated are moved through a series of process tanks. Each process bath is usually followed by a rinse tank to remove residual process solution from the part and prevent cross contamination.

The actual plating operations are preceded by a series of cleaning and surface preparative steps. Following plating, a part may undergo a number of post-treatments such as conversion coating.

The electroplating process is essentially an oxidation-reduction process; the part to be plated is the cathode and the plating metal is the anode. The metal ions in solution are usually replenished by the dissolution of metal anodes. When replenishment is with metal salts, the anodes are made of an inert material. Although there are hundreds of electroplating solutions, only a limited number of baths enjoy widespread commercial usage for any particular metal or alloy.

The most common methods for plating parts are in barrels or on racks. Barrel plating is used for coating small parts that tumble freely in rotating barrels. Parts can be rack plated by attaching them to frames.

As with other metal finishing processes, surface preparation constitutes a very important part in the overall electroplating sequence. Surface preparation involves cleaning, descaling, degreasing, and various other techniques. Choice of cleaning methods depends on the nature of the substrate and the extent of contamination. For example, ferrous and non-ferrous materials generally require different type of cleaners. Adequate rinsing between all steps in cleaning as well as plating is of the utmost importance.

All electroplating operaitons, including cleaning, plating and postplating, can be carried out manually or with almost any desired degree of automation.

Plating solutions, with a few notable exceptions, are aqueous and are either acid, neutral or alkaline. Therefore, for satisfactory operation of most baths, close pH control is essential. Some agitation of the plating solution or of the workpiece is beneficial. Each plating bath gives optimum results within a well defined temperature range. Other important parameters affecting plating efficiency include current densities at the anode and cathode, and throwing power of the bath.

Plating processes are also sensitive to the presence of impurities. Undesirable elements can be removed by such techniques as filtration, adsorption or chemical treatment. All plating baths require some form of chemical control and proper adjustments as dictated by operating conditions.

Deposits from most plating solutions produce a mat finish unless the substrate is bright and the plate is very thin. A bright appearance can be imparted after plating by various mechanical treatments, e.g. buffing. However, it is much more prevalent today to create a bright appearance by adding small amounts of brighteners to the plating bath. These brighteners are usually organic compounds. There is a vast array of brighteners on the market, and most are proprietary.

2.1 Common Metals

2.1.1 Aluminum Electroplating

Commercial uses of aluminum plating are rare. The only important application is the plating of steel for corrosion protection. Since aluminum is more reactive than hydrogen, it cannot be plated from aqueous solutions or any solution containing acidic hydrogen. The electrolyte employed is a fused mixture of aluminum chloride and alkali chlorides and is operated at a temperature of 175 °C using a current density of 161 A/m^2. Pure aluminum serves as the anode material.

2.1.2 Brass Electroplating

Brass, an alloy of copper and zinc, is not only one of the earliest but also one of the most widely used alloy electroplate. Although the vast majority of brass plating is for decorative purposes, brass coating also has important engineering applications, e.g. the plating of steel wire cord in tire manufacturing to ensure effective rubber adhesion. Incidentally, colour anodizing is now a serious competitor with brass plating for many decorative outlets.

Bright decorative work is generally carried out by flash plating brass over bright nickel or some other appropriate bright plate. When the workpiece is to be coloured or antiqued, or where buffing or brushing is required, a thicker brass coating is deposited.

All commercial brass plating solutions are of the cyanide type, and the brass alloy most often plated contains 70 to 80% copper. Characteristics of the solution make-up of the standard purpose bath for brass plating are depicted in Table 1. Composition of the solution for flash plating is about 65% of the standard formula.

Ammonia is added to increase the zinc content of the electrodeposit, extending the range of uniform plating and brightening the plate. Optimum temperature for plating is realized at 32°C.

Composition of the anodes is approximately the same as the alloy being plated. Anodes should be of very high purity, with minimum amounts of lead and tin.

Most substrate metals being brass plated do not require any special cleaning or preparation.

While the majority of brass plating can be accomplished by the method outlined above, higher speed solutions are necessary in situations where thicker deposits are required, e.g. wire and strip plating.

Two types of high speed solutions are in common usage and both are suitable for barrel as well as still plating. Both baths require addition reagents to produce uniform colour and provide wide plating range.

The first of these solutions is very similar to conventional brass plating but can be up to 50% higher in all constituents and is operated at a temperature of 45 to 75°C. The second is highly alkaline, fairly concentrated and operated with the typical formula shown in Table 2.

2.1.3 Bronze Electroplating

The term bronze is rather liberally used in the metal finishing industry; it may be an alloy of copper with zinc, cadmium, or tin, so long as the colour matches that of wrought bronze. True bronze, of course, is a copper-tin alloy. Bronze is plated for decorative as well as engineering applications.

The composition of a typical copper-cadmium bronze plating bath is depicted in Table 3. Cadmium which is plated out is replenished by additions of a concentrated solution of cadmium oxide in sodium cyanide when the deposit becomes copper-coloured or reddish. The deposit becomes white when an excess of cadmium is present. Excess cadmium can be removed by plating out on dummies or by adding sodium sulfide.

Copper-zinc bronze plating solution (Table 4) is similar to a brass since it deposits an alloy of copper and zinc. However, in the bronze deposition the proper ratio is 92% copper and 8% zinc. The function of Rochelle salts is to increase anodes dissolution. A light bronze is obtained when operating at room temperature while a red bronze results at a higher temperature.

Table 5 shows the composition and operating conditions of a typical copper-tin bronze plating bath. The bath yields an alloy of about 88% copper and 12% tin. Reddish deposits rich in copper tend to form at low temperature, low free cyanide and high free alkaline, while a golden to nearly white coating is obtained at high temperature, high free cyanide and low alkali content. Tin content of the plating bath is controlled by scheduled additions of potassium stannate in

appropriate amounts. Inclusion of a proprietary brightener in the solution can brighten the deposit, and the resultant plate may also be lacquered.

2.1.4 Cadmium Electroplating

Cadmium plating is widely employed to impart an attractive corrosion protective coating over base metals, particularly steel and cast iron, and is frequently applied to parts consisting of two or more metals to reduce galvanic corrosion. Very often, cadmium serves as an undercoat for zinc plating. The outstanding solderability and low contact resistance of cadmium also make it attractive for uses in the electrical industry. Since cadmium is relatively costly, only thin coatings are applied. Depending on the addition agents used, cadmium can be plated bright, semi-bright, or mat.

Cadmium is much easier to deposit evenly and smoothly than zinc. Moreover, the resistance of cadmium coatings to atmospheric and galvanic corrosion is much greater than that of zinc coatings.

Cadmium is usually plated from alkaline cyanide baths prepared by dissolving cadmium oxide in a sodium cyanide solution. The plating anodes consist of cadmium balls suspended in steel wire cages. Despite the environmental problems associated with cyanide, cadmium cyanide baths are popular because they cover completely and impart a dense, fine-grained deposit which can be made very lustrous by the use of stable brighteners.

Brighteners act by influencing the formation of the electrodeposited cadmium crystals. A wide variety of commercial brighteners, both organic and metallic compounds, are available and are largely proprietary. Included among the organic types are aldehydes, dextrin, milk, sugar, molasses and furfarol while metallic brighteners include nickel, cobalt, molybdenum, and selenium compounds. Optimum results are attained by a judicious use of both types of brighteners.

Several non-cyanide cadmium plating baths have also been developed, e.g. neutral sulphate, acid fluoborate, and acid sulphate. Brighteners, as required, can also be added to these non-cyanide formulations.

Table 6 depicts the composition and operating conditions of typical cyanide and non-cyanide cadmium electroplating baths.

Following plating, the parts are rinsed. In most instances no further post-treatment is applied, but sometimes a bright dip in a solution of nitric or chromic acid is carried out. In situations where it is important to minimize the formation of "white rust" or to enhance paint adhesion, chromate conversion is provided.

2.1.5 Hexalvent Chromium Electroplating

Chromium is the final finish on a multitude of plated items and is almost exclusively plated from a hexavalent chromium bath. It is applied chiefly onto steel, nickel-electroplated steel and nickel-electroplated zinc. Chromium plating can be grouped into two general categories, namely decorative and hard.

In the former, a thin chromium layer of about 2.5×10^{-5} to 5×10^{-5} cm serves as a protective, nontarnishing, durable surface finish. Since it is difficult to attain dense, pore-free chromium deposits in fine layers, chromium is usually plated over a coating of nickel or a combination of nickel and copper. Typical items coated with decorative chromium include exterior and interior automotive parts, boat hardware, household appliances, furniture for homes, offices and schools, plumbing fixtures and bicycle hardware.

Hard chromium plating, also called industrial or engineering chromium plating, is fundamentally the same as decorative chrome plating but the coatings provided are much thicker, i.e., 2.5×10^{-4} to 5.1×10^{-2} cm or more. Unlike decorative chrome, hard chromium is applied to the base metal without an intermediate coating. Engineering chromium is utilized for its great hardness and excellent bearing properties. Restoration of original dimensions of worn, mismachined or undersized parts; coating of tools, dies and gauges; coating of electrotypes, and engraving plates are some of the main outlets for hard chrome plating.

Chromium can be electroplated in still tanks, barrels and in automatic equipment.

The conventional solution for electroplating chromium contains two basic constituents : chromic acid and the sulphate ion introduced as sulphuric acid or a sulphate salt. The sulphate serves as a catalyst. More modern baths contain a mixed catalyst using a combination of sulphate ion and a fluoride or silicofluoride ion. Some typical plating bath compositions and operating conditions are depicted in Table 7.

Unlike some other plating operations, an insoluble anode is employed and chromium is replenished by the addition of chromic acid. The most popular anode materials are lead or lead alloys, especially 7% tin.

Plating baths using trivalent chromium have also been developed, but have had only limited commercial success. These baths are very sensitive to metallic impurities.

2.1.6 Copper Electroplating

Copper electroplating has a myriad of uses and consequently it is very widely employed. Although sometimes copper is electroplated as a final finish, most often it serves as an undercoat for other metals. For example, copper is universally used in plating on zinc-base die castings as the base for further coatings. Copper may be deposited mat, or with appropriate brightening agents, either semi-bright or fully bright. The deposits can be readily buffed to a high luster. Still tanks, barrels and automatic equipment can all be used to plate copper.

Copper can be electroplated from numerous electrolytes, open as well as proprietary, but four main types, namely alkaline cyanide, alkaline pyrophosphate, acid sulphate, and acid fluoborate, account for the bulk of commercial plating. The applications of various copper plating solutions overlap somewhat; however, each has fairly defined areas of usefulness.

Typical compositions and operating conditions for copper cyanide baths are presented in Table 8. Major applications of cyanide baths are for copper striking steel to further plating with acid copper and for the initial plate on zinc die

castings. In the Rochelle bath the presence of Rochelle salts permits higher operating current densities. Still higher speeds of operation are possible in high speed baths in which some or all of sodium salts are replaced by potassium.

Copper sulphate baths are employed in printed circuits, electronics, rotogravure, electroforming, decorative, and plating on plastics applications. Plating with copper sulphate has a number of advantages, e.g. low cost, easy control, and rapid deposition. Moreover, the effluents generated do not pose any particular problems to treat.

Standard formulations for copper sulphate baths along with high throw bath are depicted in Table 9 Baths can be prepared by dissolving copper sulphate in water and then adding sulphuric acid. Copper sulphate serves as the source of copper ions, replenished from the anodes. The anodes are phosphorized, oxide-free, high purity rolled copper. Sulphuric acid not only increased the conductivity of the solution but also reduces anode and cathode polarization.

Since copper fluoborate is very soluble, copper fluoborate baths allow the use of higher current densities and increased plating speed. Normally these baths do not contain organic additives. Characteristics of typical high and low concentration copper fluoborate baths are shown in Table 10.

The chief uses of copper pyrophosphate baths are for electroforming, plating on plastics, and printed circuit boards. These baths require more control and maintenance than the cyanide baths. Free or excess pyrophosphate is essential for the operation of the bath in providing conductivity and anode dissolution. Anodes, which can be copper slabs or copper nuggets in titanium baskets, must be of high purity, oxide free copper. Copper pyrophosphate solutions are sensitive to contamination, especially to organic contamination, e.g. oil or breakdown of organic additives.

The copper pyrophosphate plating bath formulation depicted in Table 11 can be utilized for all plating applications except printed circuits. Typical printed circuit bath formulation is shown in Table 12. Proprietary or non-proprietary additives improve the throwing power and ductility of the deposit.

2.1.7 Iron Electroplating

Iron plating is a rather uncommon operation due to the poor metallurgical properties of electrodeposited iron. Unless some unique property of iron, e.g. magnetism, is required in the deposit, there are better alternatives. However, iron plating does find usage in such applications as building up heavy deposits on worn parts, for printing plates, for electroforming, for surface hardened tools, dies and cylinder liners, and in some cases as a substitute for nickel. Iron may be deposited as a hard and brittle or a soft and ductile coat.

Iron plating solutions are stable and simple to operate. Numerous plating baths have been developed; all contain iron in the ferrous oxidation state. Included among the baths used are the chloride, fluoborate, sulfamate, and sulphate baths. Typical formulations of iron plating baths are depicted in the Table 13. Moreover, it is recommended that a wetting agent be incorporated into the solutions to eliminate pitting.

Chloride baths provide the best deposits. High conductivity, high permissible current densities or fast plating rates, and relatively strong, ductile and smooth deposits are the chief advantages of the chloride bath.

Sulphate plating baths are suitable when plating speed is not important and lower operating temperatures are desired. As indicated in Table 13, there are several varieties of sulphate baths: a bath which is prepared with ferrous sulphate, the so-called double sulphate bath containing ferrous ammonium sulphate, and the mixed sulphate-chloride bath which contains ferrous sulphate and ferrous chloride.

The fluoborate bath possesses a high conductivity. However, current density declines with decreasing pH, and organic contamination results in a brittle and stressed deposit.

While similar to sulphate solutions, the sulfamate bath can be operated with higher cathode current density. Characteristics of the deposit with respect to stress and hardness are similar to those from other iron plating formulations.

2.1.8 Lead Electroplating

Although relatively inexpensive and easy to plate, lead is not commonly used for electrodeposition because of its high toxicity and because the deposit cannot be used for corrosion protection of steel. Lead plating, however, is employed in the production of electrodes for lead acid batteries. Due to lead's outstanding resistance to hydrofluoric and sulphuric acid, protective linings in containers, etc. often consist of plated lead. Other applications include the coating of some types of nuts and bolts as well as bearings. Moreover, electrodeposited lead often serves as an undercoat for indium plating.

Most commercial electroplating of lead is carried out using lead fluoborate bath. Table 14 depicts typical bath composition along with operating conditions for still and barrel plating.

For the plating of bearings an alloy comprised of 7% tin and 93.9% lead is also widely used. The plating solution is identical to the lead fluoborate bath above with the exception of a 4.6% addition of stannous fluoborate by volume. The anodes used are 7% tin - 93% lead.

2.1.9 Tin-Lead Electroplating

Bath composition of tin-lead alloy can be varied to give a tin-lead coating in any desired proportion; e.g. the widely used 60:40 tin:lead solder deposit. Electrodeposited coating of 60% tin - 40% lead is popular in the electronics industry for coating the conductive tracks of printed circuit boards, protecting their solderability and also serving as an etch resist in the manufacture of the board.

Solder plating solutions are similar to those for lead plating and are prepared from liquid concentrates of stannous fluoborate, lead fluoborate and fluoboric acid. The boric acid serves as a stabilizing agent. Moreover, the presence of an addition agent, e.g. liquid peptone, is critical in the operation of the bath to promote a uniform grain structure in the plate.

2.1.10 Nickel Electroplating

Nickel ranks as one of the most important metal coatings applied by electroplating. It is plated in all thicknesses from a mere flash to many millimeters, and can be electrodeposited in still tanks, barrels, and in a variety of automatic equipment. Nickel plate, with or without an underlying copper strike plate, is chiefly employed as a bright coating underneath a relatively thin chromium electroplate. By itself, nickel is electrodeposited on steel and other base metals to provide decorative and corrosion resistant finish. To build up more parts or provide wear resistant surfaces, heavier nickel deposits are applied. Nickel plating is widely used to electroform articles having an intricate shape that would be difficult or costly to fabricate by conventional metal-working or machining techniques.

Many different nickel plating baths, each with its own set of advantages and disadvantages, are available. Nickel can be electroplated from Watts (sulphate-chloride-boric acid), sulfamate, fluoborate, and chloride solutions. The most widely used bath is the Watts bath, but sulfamate and fluoborate solutions also enjoy widespread popularity. Typical compositions for nickel plating baths are depicted in Table 15. The plating solutions also contain a small concentration of a wetting agent and brighteners as required. For example, organic compounds that refine the grain size of the deposit and brighten the plate are added to all nickel plating baths adopted for sequential nickel-chromium plating. There are numerous commercially available brighteners and are almost exclusively proprietary. As far as anodes are concerned, expanded or perforated titanium anode baskets filled with nickel of a selected size are practically standard in the industry.

The constituents of the Watts bath are nickel sulphate, nickel chloride, and boric acid. Nickel sulphate is the principle source of nickel ions, nickel chloride improves anode corrosion and increases conductivity, and boric acid helps to produce smoother, whiter, more ductile deposits. Surface uniformity of electrodeposited nickel and minimization of pitting is ensured by the use of anionic anti-pitting or wetting agents, e.g. sodium lauryl sulphate.

When nickel is plated directly on the base metals, the base metal surfaces are first cleaned, rinsed and then acid dipped and rinsed before nickel plating. As mentioned previously, the base metal is often copper plated prior to nickel plating; as a matter of fact, such a procedure is almost always employed with zinc and zinc alloy components. After copper plating, the workpieces are rinsed, acid dipped, rinsed, nickel plated, rinsed and then dried.

2.1.11 Tin Electroplating

Tin is one of the easiest metals to electroplate. The coatings obtained are non-toxic, ductile, and resistant to corrosion as well as tarnishing. Tin plating operations can be carried out with minimal control. Unlike hot tin dipping, tin plating permits accurately controlled and uniformly thick coatings. Unusual shapes can be readily plated owing to the high throwing power of tin. Major baths available for commercial use are the alkaline stannate, acid sulphate, acid fluoborate, and bright-tin acid.

The alkaline stannate bath can be formulated with either sodium or potassium salts. However, potassium stannate is generally preferred because of its greater conductivity, higher plating speed, and less tendency for sludge formation. Both types of baths yield smooth, mat deposits without the need for additional organic reagents. Anodes may be made of pure tin, a tin alloy of 1% aluminum, or inert materials, e.g. steel or nickel. Use of insoluble anodes avoids such potential problems as anode filming. With inert anodes, the bath has to be replenished chemically; this can be met by adding a tin oxide solution.

Composition and operating conditions for stannate baths are depicted in the Table 16.

High current efficiency, high cathode efficiency, operation at room temperature, and ease of control are the outstanding characteristics of the stannous sulphate bath. This electrolyte contains stannous sulphate plus sulphuric acid and cresosulphuric acids, with additions of gelatin and B-naphthol (or other proprietary organic additives) to ensure smooth, fine grained deposits and to increase the throwing power of the bath. Barrel plating is one of the common uses of the acid sulphate bath.

The stannous fluoborate bath can be adapted to rack, barrel, wire and strip plating over an extremely wide range of current densities at room temperature or slightly above.

The bath contains stannous fluoborate, fluoboric acid, plus gelatin and B-naphthol, or proprietary organic additives. Addition agents are incorporated into all stannous fluoborate solutions to improve throwing power and to produce fine grained deposits. The plate is whiter than that from alkali stannate baths. Moreover, the fluoborate bath consumes as little as 10% of the electricity of a stannate bath, and its plating speed is two to three times as fast as that of a stannate solution.

The bright tin acid bath is basically the acid sulphate bath with alternative organic additives to ensure a finer grain size and a consequent bright deposit. These organics include acetaldehyde and formaldehyde as well as proprietary brands developed for specific uses, e.g. continuous strip plating.

2.1.12 Tin-Nickel, Tin-Copper and Tin-Zinc Electroplating

In addition to tin-lead, other important tin alloys which are electroplated are tin-nickel (65% tin - 35% nickel), tin-copper (10 - 15% tin), and tin-zinc (75% tin - 25% zinc).

Tin-nickel may be electroplated directly on base metals such as steel, copper, brass and on an undercoat of copper or nickel on zinc base die castings. Plating may be carried out from fluoride or pyrophosphate baths. One of the major outlets for tin-nickel plating is in the automotive industry for disc-brake pistons because of its good wear and corrosion resistant properties. Other applications include brewery equipment (e.g. taps and other fittings), heavy duty electrical fittings, decorative finishes for instruments, and tags and connectors in the electronics industry.

Tin-copper, or "red bronze", can be electroplated from solutions of sodium or potassium stannate, and cuprocyanide, at 60°C. Steel hydraulic pit props, cast

iron pumps and motors used in aircraft, and as a "gold-like" finish on jewelry and watches are some of the principal uses of tin-copper plating.

Although tin-zinc coatings can be electrodeposited over a range of compositions, the greatest corrosion resistance is exhibited by alloys containing 20 to 35% zinc. The deposit is produced from an alkaline stannate/zinc cyanide bath and is mat with a silvery-white colour. Since it offords greater protection to steel than does cadmium in industrial atmospheres, it often serves as an alternative to cadmium coatings.

2.1.13 Zinc Electroplating

Zinc is popular for electroplating parts not only because it is a relatively inexpensive metal but also because it provides good protection against outdoor as well as indoor corrosion. Zinc is the preferred choice to coat numerous ferrous items; as a matter of fact, zinc electroplating is now the most common technique for affording corrosion protection to nuts and bolts. Moreover, the electrical and electronics industries along with the communications industry are especially large users of electrodeposited zinc. Electroplated zinc seldom has a thickness greater than 0.027mm and is usually slightly more than 0.0075mm. Zinc can be readily applied in tank, barrel, or continuous plating facilities.

Zinc is electroplated in:

1. cyanide solutions containing sodium cyanide, zinc oxides or cyanide and sodium hydroxide.
2. non-alkaline solutions prepared with zinc pyrophosphate or another chelating agent such as tetrasodium pyrophosphate, sodium citrate or the sodium salt of ethlenediamine tetraacetic acid (EDTA).
3. acid or neutral chloride baths prepared with zinc chloride and a buffer salt such as ammonium chloride.
4. acid sulphate solutions containing zinc sulphate and a buffer salt such as aluminum chloride or sulphate.
5. other acidic electrolytes, e.g. fluoborate and sulfamate solutions.

Cyanide solutions may be high, medium or low strength. Regular or standard, i.e., high, cyanide baths are the most trouble-free of all zinc plating baths to operate. However, mid-strength baths perform closely to the regular bath, and consequently most zinc cyanide plating is carried out using these type of baths. Typical composition and operating conditions for zinc cyanide baths are shown in Table 17.

Neutral and acid chloride baths are proprietary, requiring several additives. Low cyanide and acid zinc solutions require more control than high cyanide baths to ensure the attainment of a satisfactory deposit. Deposits from acid zinc baths are slower than with the high cyanide solution, but the effluent problem is considerably less severe. As a matter of fact, non-cyanide baths were developed to a large extent to avoid treating cyanide wastes.

Fabricated steel parts coated with zinc are plated in cyanide baths. The application of acid zinc solutions is largely confined to the plating of mill products such as wire, strip, sheet, and conduit.

Cleaning of ferrous metals prior to zinc cyanide plating consists of electrolytic cleaning, rinsing, acid pickling, rinsing, and cyanide or caustic dipping.

When zinc plated parts are not given any post-treatment, they are simply rinsed in cold water, then in hot water and finally air dried.

Zinc plated parts can be post-treated by bright dipping in a dilute nitric acid solution or chromated. By chromating immediately after deposition of the zinc, an increase in the corrosion resistance is obtained which almost equals that of the original deposit. Chromating also enhances the adhesion of paint to zinc-plated parts. Therefore, chromating is now almost universally applied to zinc plated workpieces.

2.2 Precious Metals

2.2.1 Gold Electroplating

Gold plating is widely used where appearance and corrosion resistance are of paramount importance. Thus gold is employed as a decorative coating on jewelry, watches, novelty items, and the like. Because of gold's low contact resistance, high solderability and ability to withstand corrosion, gold plating is also an important process in the electronics and electrical industries.

There are a tremendous number of gold plating solutions, yielding deposits having a wide variety of characteristics. In addition to plating pure gold, frequently a number of alloying elements, e.g. cobalt, indium, silver, cadmium etc., are used in gold plating baths at varying concentrations in order to obtain specific physical properties in gold deposits. The alloy content in these gold baths is very low and has negligible impact on the parameters of gold plating.

Although it is possible for a plater to prepare gold plating baths from published sources, most platers rely on proprietary gold plating solutions available from suppliers.

The majority of gold plating operations are performed using cyanide solutions., Cyanide baths can be divided roughly into three types, i.e., alkaline, neutral and acid. Of these, the acid baths are regarded the most versatile. Typical compositions and operating conditions for gold cyanide plating baths are depicted in Table 18.

A number of noncyanide baths are also available, and one based on a sulfide complex has attained widespread acceptance.

2.2.2 Indium Electroplating

Indium is a soft metal, similar in colour and luster to platinum. Because it is expensive, indium is used only when necessary and is often alloy plated with copper, tin, lead, cadmium, bismuth or rhodium. The friction and corrosion resistance characteristics of indium are unique.

Indium plating is widely utilized for very high rated bearings, e.g. aircraft engine bearings. In these applications, the indium is plated and diffused on the bearing surfaces to impart a low coefficient of friction, good resistance to corrosion, and a first class anti-seizure property. Electroplated indium coatings also provide low resistance contacts on, in particular, aluminum electric wiring.

Indium can be plated from cyanide, sulfamate, fluoborate or sulphate solutions. Typical compositions and operating conditions are depicted in Table 19.

The cyanide bath is employed when extremely high throwing power and adhesion are called for. Deposits are uniform and bright mat in appearance. However, due to the high pH of the bath, insoluble anodes (i.e. steel anodes) are required, necessitating replenishment in the form of an indium cyanide concentration.

Sulfamate baths are very stable and easy to operate and control. Unlike the cyanide bath, the sulfamate bath utilizes soluble indium anodes. Throwing power of the bath is comparable to the cyanide bath. Sulfamate baths also give deposits which are uniform and bright mat in appearance.

The fluoborate bath employs pure indium anodes and yields a fine grained deposit. Low cathode efficiency is one of the shortcomings of this type of bath.

2.2.3 Platinum-Group Metals Electroplating

Rhodium is the most commonly plated metal among the platinum group metals (i.e., platinum, rhodium, palladium, osmium, ruthenium and iridium). It is plated for decorative purposes on silverware, jewelry, watches etc., and to enhance the colour of gold and gold-filled products. On silver items, rhodium preserves the

luster of silver and protects it from tarnish. The electrical and electronics industries also make use of plated rhodium. High hardness, excellent corrosion resistance, low electrical contact resistance, good heat and wear resistance, and high reflectivity are some of the outstanding characteristics of rhodium deposits.

Decorative coatings are very thin, on the order of 0.1μm. When the base metal is not silver, gold or an alloy of these metals, an undercoat of nickel is generally applied. Incidentally, the electroplating of gold or silver with a very thin coating of rhodium is termed rhodanizing. While thin deposits are adequate for most decorative work, much thicker deposits are required for wear and corrosion resistance; i.e., deposits having a thickness of about 25 μm.

Rhodium plating baths are supplied as phosphate or sulphate concentrates. Since the plating operations use inert anodes, e.g. platinized titanium, the baths are replenished chemically. Composition of typical sulphate and phosphate plating solutions along with operating conditions are summarized in Table 20.

Because of its excellent corrosion and tarnish resistance, electroplated platinum is a popular decorative coating, especially on jewelry. However, platinum can often be substituted in these applications by the less expensive rhodium. Platinum plating also has uses in the printed circuit industries.

There are several baths for plating platinum in an acidic solution having a nominal metal concentration of 5 g/L which operates at a temperature of 30 °C.

Palladium, the least noble of the platinum metals group, can be electrodeposited from chloride or bromide solutions and from a molten cyanide bath. Because palladium is cheaper than gold or platinum, the main use of palladium is as a substitute for these metals as a decorative coating on jewelry and the like. Electroplated palladium has also found some applications in the electronics industries.

Although ruthenium, iridium and osmium can be electroplated, commercial applications of the first two are rare and nonexistent for osmium.

Thin coatings of ruthenium may be electrodeposited on a suitable base coat. Plating on silver, copper or nickel is preceded by a flash deposition of gold. Plating baths are based on nitrozyl chlorides or nitrosyl sulfamates, and the metal is electrodeposited at elevated temperatures and low current efficiencies.

2.2.4 Silver Plating

Silver is the most common deposit for tableware and decorative household articles, and is a widely used coating on many types of jewelry. Electroplated silver has also found applications for use on bearings and in the electronics and related industries. Incidentally, many military specifications forbid the use of silver in miniature circuit boards because under certain conditions silver can migrate across insulation.

Silver is electrodeposited from cyanide baths exclusively and has the best throwing power of any electrodeposit. Generally a two-step process is employed in silver plating; a strike in a bath low in silver and high in cyanide followed by a regular silver plating bath to build up the deposit to the desired thickness. For most purposes deposits of approximately 0.025mm are satisfactory. To prevent electroless deposition and poor adhesion in the plating of silver on steel, an underlay of copper or nickel is required between the silver and the steel.

The traditional formula for rack or barrel work is shown in Table 21.

The anodes must be of very high purity silver to avoid anode filming which inhibits proper dissolution.

3.0 IMMERSION PLATING

When the substrate metal is less noble than the plating metal, or can be made so by the use of appropriate complexing agents in the solution, a thin layer of immersion deposit may be formed. Immersion processes are advantageous because of the virtually unlimited throwing power, and low capital costs involved due to the fact that no source of dc power is required. However, since the reaction stops as soon as the substrate is completely covered, immersion deposits generally cannot be built-up to thickness obtainable by electrolytic techniques. The thickness of immersion deposits is usually of the order of 0.25 μm, although some processes can yield deposits as thick as 2.5 to 5.0 μm. Thinness of the coatings limits the usefulness of immersion deposits to decorative coating or preparation for further processing, e.g. painting.

The most important immersion plating processes are: 1) tin on brass, copper, steel, or aluminum, 2) copper on steel, 3) gold on copper or brass, 4) nickel on steel, and 5) zinc on aluminum.

For example, immersion tin plating is employed to "whiten" pins, hooks, eyelets, screws, buttons, and other hardware items made of copper, brass, or steel. Immersion in alkaline stannate solutions to deposit tin on aluminum alloy pistons is widely practised by all the leading automotive manufacturers. Copper is immersion deposited on steel wire prior to drawing in order to lessen wear on the dies. Some types of inexpensive jewelry are gilded by immersion depositing in gold. Nickel is immersion deposited on steel prior to ceramic enameling to enhance adhesion of the enamel.

Other metals which can be immersion deposited on various substrates include : 1) cadmium on aluminum, copper alloys, and steel, 2) lead on copper alloys, steel and zinc, 3) silver on zinc and copper alloys, and 4) palladium, platinum, rhodium or ruthenium on copper alloys.

There are a vast multitude of immersion plating bath formulations; for example, immersion solutions for depositing tin on aluminum, copper alloys, steel and zinc are depicted in Table 22.

4.0 CHEMICAL CONVERSION COATING

4.1 Phosphating

Phosphating is the treatment of a metal surface to produce a coating of insoluble metal phosphate crystals which strongly adhere to the base material. Typical thicknesses range from 0.0025 to 0.005 cm and may vary in colour from light grey to black. Phosphate coatings are widely applied onto ferrous materials as well as zinc, cadmium, aluminum and magnesium-based metals. The process is of major importance in a number of industries, especially the automotive and appliance industries.

Phosphate Coatings :

1. precondition surfaces to receive and retain paint and other organic coatings,

2. prepare surfaces for bonding with plastic or rubber,

3. improve corrosion resistance of the metal surface by the coating itself or by providing a suitable base for rust-preventative oils or waxes,

4. condition the surface for cold forming operations by providing a base for drawing compounds and lubricants.

For example, paint does not adhere well to zinc surfaces without prior treatment. As a matter of fact, the largest use of phosphate coatings is to provide a base for bonding paint to metal.

Phosphate coatings can be carried out by brush, spray or immersion methods employing manual or automatic machine techniques which may be applied to single or batch lots of work pieces.

A typical commercial phosphating cycle consists of cleaning the metal surface, applying the phosphate coating, followed by a hot water rinse and a final rinse in a passivating solution, e.g. a 1% by volume chromic acid. In some cases the rinse steps may be followed by a dip in a suitable oil, wax or other lubricant before drying in hot air.

Commercial phosphating preparations are complex, proprietary mixtures. Each type of phosphate coating has a unique set of characteristics and area of application. Present day phosphating solutions contain one or more of the phosphates of iron, manganese or zinc in dilute phosphoric acid. The formulations may also include the phosphates of alkali and alkaline-earth metals plus compounds which act as accelerators. Accelerators commonly used include nitrates, nitrites, chlorates and peroxides or combinations of these. Nitrite accelerators are especially popular.

Iron, zinc, zinc-calcium and manganese phosphates are widely utilized as underpaint coatings for steel. Stampings for cabinets and metal furniture generally receive iron phosphate coatings. For automotive bodies, refrigerators and various appliances, zinc phosphates and zinc-calcium phosphates are the usual choices. Heavy zinc phosphates and manganese phosphates are employed on hardware, nuts, guns, bolts, and the like. These latter types are often supplied in conjunction with protective oils and waxes. To aid in drawing and cold forming of metals, manganese phosphates and zinc phosphates are the predominant choices.

4.2 Colouring

Metal surfaces can be coloured to a wide variety of pleasing shades by a host of different techniques. The colouring of anodized aluminum, for example, has already been described in one of the previous sections. Although the primary purpose of colouring metals is for aesthetic value, colouring can also impart other favourable properties, e.g. enhanced resistance to corrosion, abrasion, or wear resistance.

Chemical conversion methods of colouring whereby the metal surface is converted into an oxide or other insoluble metal compound constitute one

important colouring technique. The most common coloured finishes are applied onto copper, steel, zinc, and cadmium.

Colour is imparted to the cleaned base metal by a brief immersion in a dilute aqueous solution. Many formulations are available; the majority are proprietary. Since the coloured films are extremely thin and delicate, they are usually protected by a coat of lacquer applied by spraying or dipping.

Foremost among the oxide-film forming processes for steel are the alkaline blackening treatments. The treating bath consists of a strong alkaline solution containing oxidizing agents such as nitrites, nitrates, or chlorates. Colour and other characteristics of the casting obtained are largely a function of the steel being treated, its surface properties, concentration of the bath, and temperature and time of immersion.

A grey colour can be given to silver by immersion in a polysulfide solution such as ammonium polysulfide.

By immersion in a solution of nitric acid and copper sulphate, tin can be darkened to obtain an antique finish of pewter.

Various colours can be imparted onto zinc; for example, in a solution of ammonium chlorate the colour sequence is yellow, brown, violet, deep blue, and blue black depending on the length of immersion in the colouring solution. On the other hand, ammonium molybdate solutions give a gold to brown to black colour sequence.

4.3 Chromating and Passivating

Chromate conversion coatings are protective films formed on metal surfaces. During chromating, a portion of the base metal is converted to one of the components of the film by reaction with aqueous solutions containing chromic acid or its potassium or sodium salts, plus organic or inorganic compounds such as activators, accelerators, or catalysts.

Chromate conversion coatings are generally applied by a chemical immersion, spray, or brush treatment. Chemical or electrochemical methods can also be utilized to apply such coatings.

Zinc, cadmium, aluminum, magnesium, copper, brass, bronze, and silver are the metals most commonly subjected to chromating.

Chromating has little permanence with steel, but will add to other forms of corrosion prevention and is generally used following phosphating and as an additive to zinc-rich primer paints.

Chromate treatments generally employ proprietary solutions. A wide variety of protective and decorative films can be produced. Appearance of the coating will be determined by the base metal and the processing technique used. Further colouring of the coatings can be attained by dipping the work pieces in organic dye baths. Chromate coatings are not only utilized as protective or decorative films but also to provide an excellent base for paint and various other organic finishes.

Chromating is often referred to as passivation, but strictly speaking, other techniques unrelated to chromating also use this term. Passivation may be defined as process for metals whereby an increase in corrosion resistance is achieved by chemical or physical means, i.e. the metal is made less reactive. Thus chromating is a form of passivation. Another example of passivation is the immersion of nickel and some of its alloys in concentrated nitric acid followed by washing and drying to produce an oxide film which improves the acid resistance of the nickel.

5.0 ELECTROLESS PLATING

Electroless plating is a chemical reduction process which depends upon the catalytic reduction of a metallic ion in an aqueous solution containing a reducing agent, and the subsequent deposition of the metal on the workpiece without the use of external electrical energy. The base substrate being plated must be catalytic in nature. In the electroless plating process a properly prepared workpiece provides a catalyzed surface and, once introduced into the electroless solution, a uniform deposition begins.

Electroless deposition can give films of metals, alloys, compounds and composites on both conductive (e.g. metals) and non-conductive (e.g. plastics, glass, ceramic) surfaces.

Electroless plating on metals is generally associated with products that have to withstand unfavorable conditions or significant wear and abrasion.

Electroless plating on plastics is used in the automotive, appliance, cosmetic, electrical, hardware, furniture, and plumbing industries. Plastics most widely employed for electroless plating include ABS, polycarbonate, polypropylene, polysulfone, and epoxies. Virtually all the electroless plating done on plastics is followed by some form of electroplating operation.

Applications for electroless plating on glass include the manufacture of mirrors and various architectural glasses. Ceramic resistors and ceramic circuit boards are some of the ceramic items coated through the use of electroless baths.

Although electroless plating is utilized in the production of numerous goods, printed circuits represent the most diverse field of electroless plating.

A number of unique advantages can be realized with electroless plating compared to conventional electroplating; for example, electroless plating imparts an even plating thickness on all areas of the workpiece regardless of the configuration or geometry of the part. Furthermore, electroless plate is dense and virtually nonporous, and certain types of electroplates provide superior hardness and corrosion protection than their electroplated counterparts.

Any metal that can be electroplated can theoretically be deposited by electroless plating. However, only a few metals - most notably nickel and copper and to a lesser extent gold, silver, palladium and cobalt - are used on any significant scale.

Basic ingredients in an electroless plating solution are: a source of the metal, usually a salt; a reducing agent; a complexing agent to hold the metal in solution to prevent indiscriminate plating out of the metal; and various buffers and chemical additives to maintain plating stability and to prolong bath life.

The source of nickel in an electroless nickel bath is a salt such as nickel chloride or nickel sulphate. Sodium hypophosphite serves as the reducing agent while the most widely used complexing agents are citric acid and glycolic acid.

In electroless copper plating the source of copper is a salt such as cupric chloride or copper sulphate. Formaldehyde is by far the most common reducer; others which can be employed include acetaldehyde, trioxane, hydrazine and hypophosphite. The complexing agent is usually either a tartrate (Rochelle salt) or a member of the amine family.

One of the drawbacks associated with electroless plating from an environmental viewpoint is the presence of complexing agents. Complexing agents make conventional precipitation of metals from wastewaters very difficult; the usual procedure is to destroy the complexes in order to free the metals for precipitation.

As indicated previously, surface preparation is a very important step in the electroless plating process.

Surface preparation of metals consists of cleaning by vapour degreasing and alkaline cleaning to remove oil and grease from the surface, then acid cleaning to remove oxide and scale, followed by electrolytic cleaning, and a final cleaning to remove light oxide films and to activate the surface for flash electroplating. The electroplate acts as a catalyst for the subsequent electroless plating process.

The initial steps in the surface preparation of electroless plating on plastics consists of alkaline cleaning and roughening. Roughening can be carried out by mechanical methods such as tumbling or vapour blasting or by chemical means such as etching with an acid. This is followed by neutralization. Catalysis by a stabilized reaction product of stannous chloride and palladium chloride follows neutralization. After the catalyst is applied, the part is immersed in the electroless bath and the desired metal plates out on the palladium. The initial layer of metal deposited becomes the catalyst for the remainder of the plating process.

Although copper and nickel are by far the most important metals deposited by electroless plating, gold, palladium, silver and cobalt have also found specialized applications.

For example, gold electroless plating is widely used in the electronics industry. Electroless gold can successfully be applied to nickel, nickel alloys, electroless nickel, copper, copper alloys, electroless copper and metalized ceramics. Furthermore, it can be deposited onto already present thin electrodeposited gold for additional strength.

Electroless palladium plating is used chiefly in the electronics industries as a less costly alternative to gold plating of electronics components, connectors and circuit boards. Electroless palladium plating without a gold overplate is cost effective, it provides equivalent or improved performance over gold finishes, and is especially ideal for contacts undergoing flexing.

Electroless cobalt deposits are utilized in the electronics industry on thin film memory dises and storage devices primarily for their magnetic properties.

Production of mirrors constitutes the major application for electroless silver.

6.0 ANODIZING

Anodizing is an electrolytic treatment of aluminum whereby the metal or its alloy is coated with about 2 to 20 μm thick artificial oxide film, resulting in longer life for the metal in addition to improving its appearance, reflectivity, and various other characteristics. The process is carried out in an aqueous electrolytic cell with the aluminum work piece serving as the anode. Oxygen is provided by the electrolytic dissociation of water.

Sulphuric, chromic, oxalic, and phosphoric acid electrolytes are the base for almost all industrial anodizing processes. Of these, the most important commercial process is sulphuric acid anodizing. All of these anodizing techniques employ the same type of equipment.

Following anodizing, the work piece may be directly sealed or coloured and then sealed.

Sulphuric acid anodizing is characterized by low cost, rapid action, and comparatively low operating voltage. A wide range of thicknesses, hardness and porosity may be produced by varying the acid concentration, operating temperature, and retention time. For example, use of low acid concentrations and temperatures favour less porous, harder oxide coatings, while increased solution temperatures and anodizing times favour more porous, even powdery coatings. A typical process involves a 15 - 20% solution of sulphuric acid with anodizing times of 20 to 40 minutes at a temperature of 15 to 25 °C. Cathodes may be made from lead, aluminum or stainless steel.

A much thicker, harder and more wear resistant coating can be produced by lowering the temperature of a conventional sulphuric acid electrolyte to 0 - 30 °C and extending the reaction time to 60 to 200 minutes. This process is called hard anodizing.

Chromic acid anodizing yields a thin, relatively soft oxide film of dark greenish or grey colouring. The bath contains 50 to 100 g/L of chromic acid ($Cr0_3$), and is operated at a temperature of approximately 35 °C with anodizing times ranging

from 5 to 20 minutes. Chromic acid anodizing is especially widely used on aircraft parts in preparation for paintings.

Oxalic acid anodizing produces a coating with a golden-yellow colour having excellent hardness and wear resistance. Although it is more expensive than the sulphuric acid method, oxalic acid anodizing can give thicker oxide coating without the need for low electrolyte temperatures. The bath contains 2 to 16% oxalic acid maintained at 16 to 29°C. Typical anodizing times are from 40 to 60 minutes.

In phosphoric acid anodizing the electrolyte employed is a 3 - 20% phosphoric acid solution operating at a temperature of 30 - 35°C. Anodizing time is usually between 15 and 30 minutes. When phosphoric acid anodizing is used as a pretreatment for electroplating, the anodized work piece must be thoroughly rinsed and the oxide coating must not be allowed to dry before plating.

There are three main techniques for colouring anodized aluminum, each of which is closely linked to the anodizing process itself. They are adsorptive dyeing, integral colouring, and electrolytic colouring.

In adsorptive or chemical dyeing, the unsealed anodized aluminum surface is immersed in a tank containing inorganic or organic dyes. Since the range of dyes and pigments available is virtually limitless, the number of colours attainable by this method is extremely large.

In integral colouring, also called colour anodizing, finely, divided particles are distributed throughout the oxide film as it is formed, using special organic acids as the anodizing electrolyte.

In electrolytic colouring, as with adsorptive dyeing, a normal unsealed anodized coating is produced first, and then small metal particles are deposited in the bottom of the pores by immersion in a metal salt solution with the passage of an alternating current. Common metal electrolytes include those of tin, cobalt, and nickel. A number of suppliers have developed and are marketing various proprietary processes for electrolytic colouring.

As mentioned above, sealing constitutes the last state of a normal anodizing sequence. It involves the sealing of the pores by immersing the work piece in hot water or a chemical solution. Sealing is required in sulphuric acid anodizing while oxalic acid processes may or may not be sealed. Chromic and phosphoric acid processes do not require sealing.

Sealing in distilled or de-ionized water at or near boiling is the simplest sealing technique. With a dichromate seal enhanced corrosion resistance is imparted to the work piece. Another common process involves sealing in a nickel-cobalt acetate solution. Table 23 depicts typical operating conditions for these three sealing techniques.

7.0 HOT DIPPED COATINGS

Low melting metals provide inexpensive protection to the surfaces of a variety of steel articles. In applying hot dipped coatings, the work piece, after thorough cleaning is immersed in a molten bath of the coating metal for a predetermined time interval. Hot dipped coatings include aluminum, zinc, lead, tin and alloys such as lead-tin and aluminum-zinc. While hardware and hollow ware are handled individually or in batches, sheet, strip and wire are processed on a continuous basis at relatively high speeds.

Hot dipping is the most widely used process of coating steel, especially plain carbon, low alloy and stainless steel, with aluminum. In the process, the aluminum bath is maintained at 680 - 720°C, and the steel is immersed for approximately 5 to 15 seconds. Upon immersion, the iron reacts quickly with the aluminum forming a highly protective aluminum oxide film. After dipping, the material is finished by jet finishing, rolling, and quenching.

Hot dipped aluminum coated (aluminized) steel products with coatings of up to 10 μm thick are particularly useful in appliance parts for their best reflective qualities. Oil refinery equipment, furnaces, and architectural components are some of the other major outlets for aluminum hot-dipped steel.

The deposition of molten zinc onto the surface of mild steel, cast iron or steel alloys is called galvanizing. Galvanized steel is used for roofing, structural shapes, automotive bodies, hardware, sheet, strip, wire products, etc. Galvanizing imparts excellent corrosion resistance; coatings of 0.01 mm will generally give a life of more than 10 years in industrial and marine environments. Since the coating obtained by galvanizing is appreciably thicker, galvanizing provides a corrosion resistance superior to electroplating of zinc.

Before steel is galvanized, it is cleaned, pickled in hydrochloric or sulphuric acid, fluxed, and dried. Since the galvanizing process is carried out at temperatures above 450°C, the steel must be thoroughly dried to avoid conversion of moisture to steam and the concomitant explosive results. The work pieces are retained in the molten zinc bath for a definite time period; if the residence time is too brief

or too long, the zinc coating will be adversely affected. When the galvanized components are to be painted, special etch treatments or etch primers are required to ensure proper paint adhesion.

Galvannealing is a modification of the galvanizing process. Upon removal from the molten zinc, the steel parts instead of cooling are maintained at a temperature of approximately 450°C, allowing the zinc to form an alloy with the surface of the steel.

Galvannealing is more expensive than galvanizing but yields a homogeneous deposit that is more attractive and improves the paint adherence characteristics of the coating. However, corrosion resistance of the deposit is somewhat inferior to the conventional galvanized coating.

Hot dipping of tin is one of the oldest coating methods, dating back to the 14th century, and is still popular today even though it has been superseded by electrolytic coating techniques in many applications. Most hot dipped tin plate is used as cans for food packaging. Hot tinning is also utilized in the electronics industry and for coating wire.

Because pure lead does not alloy well with steel, hot dipping of pure lead is a rather uncommon operation. However, terne metal, which is a combination of lead and tin containing 15 - 50% tin, is widely employed where atmospheric corrosion resistance in the absence of abrasion is required at a low cost. Thus terne plate with coatings of up to 20 μm is used in the automotive industry for gasoline tanks and in household applications for roofing and plumbing.

8.0 CHEMICAL ETCHING, MILLING & BRIGHT DIPPING

8.1 Etching, Milling and Bright Dipping

Etching and milling are processes used to produce specific design configurations and tolerances of surface appearances on parts by controlled dissolution with chemical reagents or etchants. Chemical etching and chemical milling are fundamentally the same; however, the rates and depths of metal removal are usually much greater in chemical milling than in chemical etching.

The majority of etching solutions are acidic while sodium hydroxide is used quite frequently as a caustic etch on aluminum. Typical solutions employed for chemical milling and etching include ferric chloride, nitric acid, ammonium persulphate, chromic acid, cupric chloride, hydrochloric acid and combinations of these reagents. Etching baths containing chromic acid are widely employed prior to plating, e.g. on plastics before electroless plating of copper and nickel. Etching solutions incorporating ammonia compounds, especially ammonium hydroxide and ammonium chloride are popular in the manufacture of printed circuit boards.

Bright dipping is a specialized form of etching. It is used to remove oxide and tarnish from ferrous and nonferrous materials and is frequently employed just prior to anodizing. A range of surface appearances from bright clean to brilliant depending on the surface smoothness desired for the finished part can be produced by bright dipping.

Bright dipping solutions usually involve mixtures of two or more of sulphuric, chromic, phosphoric, nitric and hydrochloric acids. For example, chromic acid in conjunction with other acids is used for the bright dipping of copper and copper alloys as well as zinc and cadmium plated parts. Other types of bright dipping solutions are also available; for example, one bright dipping formulation for silver contains a mixture of sodium cyanide and hydrogen peroxide.

8.2 Electropolishing

Electropolishing, or electrolytic polishing, is a process in which a metal serving as the anode in an electrolyte is subjected to a direct current leading to the removal of some of the metal. Thus electropolishing is a reverse of electrodeposition. The chief objective of electropolishing is to produce a bright surface having a high reflective finish. In most cases, this is done for decorative reasons. Electropolishing is often carried out in conjunction with some other forms of metal finishing, e.g. anodizing or subsequent plating or lacquering.

9.0 STRIPPING

Salvage of plated articles involves the removal of all or part of the metallic coating before reprocessing. Stripping is based on the difference in chemical activity of the difference in chemical activity of the deposited coating and the base metal. Immersion methods and the use of electrolytic solutions are the most common techniques for stripping plated metals. The former is advantageous because of its simplicity. Electrolytic stripping with hydrochloric acid can effectively remove many metals from substrates. Satisfactory stripping can be achieved using recommended solutions and procedures. However, stripping is not a simple process; as a matter of fact, stripping metallic coatings takes as much care and planning as the original plating process. For example, a particular stripping process will sometimes work for a thin deposit but not for a heavy one; or a stripping process will work for a newly plated coat and not for an old deposit. In such situations, experimenting with the stripping solution and operating variables (e.g. temperature, agitation, current density) is necessary to identify optimum conditions.

There are a host of recommended procedures for removing metallic coatings from substrates. For example, to strip copper from non ferrous metals, a solution containing sodium sulfide and sulfur can be used. Nickel can be stripped from steel by placing the parts in a mixture of nitric acid and hydrochloric acid. Anodized coatings from magnesium can be removed by retaining the work piece in a chromic acid solution for about three minutes at a temperature of 49 - 71 °C, while zinc type phosphate coatings can be removed from steel by using a solution containing caustic soda and sodium cyanide.

10.0 PRINTED CIRCUIT BOARDS

The printed circuit board is one of the most important inventions of the 20th century. These boards are used in communications, military, aerospace, business, entertainment and many other applications.

There are three basic types of printed circuit boards : single sided, double sided and multilayer. Single sided boards, which have a conductor pattern on only one side, are used for relatively simple circuitry. As its name implies, the double sided board has conductors on both sides. If there is electrical connection between the layers, it is accomplished by going through the board rather than around it, and plated-through-holes have become the conventional method of making such a connection.

Multilayer printed circuit boards have evolved from the need to accommodate increasingly complex circuitry into a limited space. Interconnections between specific conductor layers are commonly achieved by plated-through-holes, although other techniques are also available.

The number of possible variations in printed circuit board production is very large, and currently used processes are said to number more than one hundred. However, the majority of boards are manufactured by three well established production techniques, namely the subtractive, semi-additive and additive processes.

The subtractive process is the most common method for making modern printed circuit boards and accounts for about 90% of the total boards produced. Semi-additive processing was developed to reduce copper waste. The additive process is the most technologically demanding, and like the semi-additive method, can realize material savings and higher circuit densities.

In the subtractive process the starting material is a laminate already clad with copper foil and the desired conductor pattern is basically produced by removing the copper from the rest of the panel. On the other hand, in the additive process the required conductor pattern is built up on the plain substrate resin.

The subtractive process begins with a laminate board clad with a copper foil. Through-holes are punched or drilled, and the resultant holes are deburred. The board is cleaned, catalyzed and placed in a flash electroless copper bath in order to deposit a uniform conductive layer over the entire board, including the nonconductive holes.

The board is now ready for full copper electroplating. At this state, the board can be handled in one of two ways.

In pattern plating, the image photoresist is applied first, so that copper is plated only on the final track patterns, plus hole walls, avoiding build-up on areas from which it must be subsequently etched away.

In panel plating, the whole board is electroplated with copper. Then a plating resist is applied in a form such that only the desired circuit is left exposed.

Of these two options, pattern plating is the more favoured route for complex circuit boards, particularly if the conductor width is very narrow.

After copper electroplating has been carried over the tracks and on the through-hole walls by either pattern or panel plating, tin lead plate (i.e. 60% Sn - 40% Pb solder) is applied over the electroplated copper.

The plating resist is stripped off, exposing the copper in areas where the circuit is not required. By using a suitable etchant, the unwanted copper is removed. The copper circuit tracks and through-holes are protected from the etchant by the solder plate. As much as 80% of the original copper can be wasted.

If the circuit board has edge tabs or connectors that require gold plating, the tin-lead is removed from these tabs by immersing just the edge of the board in a stripping solution. This operation is followed by a nickel plating and then a gold plating treatment on the edge tabs.

Finally, the solder plate in the circuit is reflowed to completely seal the copper circuitry.

The additive process involves the deposition of plating material on the board in the pattern dictated by the circuit, rather than removing metal already deposited as in the subtractive method.

The process starts with a bare board which may or may not be impregnated with a catalyst. After making the holes, the surface is roughened or etched. If the board had not been impregnated with a catalyst, the catalyst is now applied. Next, the plating resist, outlining the required circuit pattern, is applied in the non-circuit areas. The accelerator step required for the electroless plating follows next. Heavy-build electroless coppers are used to build up the final thickness of the entire circuit. Electrolytic copper plating cannot be employed because there is no continuous conductive film linking the discrete circuit paths. After copper deposition, the tabs are plated in the same manner as in the subtractive process. Finally, various finishing steps are applied to the board.

The semi-additive process is a compromise between the additive and subtractive methods. It starts with an unclad board into which holes are drilled or punched. The board is then subjected to etching, then to catalysis and activation. Electroless copper is deposited onto the entire board surface as well as the inside surfaces of the holes. After applying the circuit pattern, the board is copper electroplated to build up the circuit to the desired thickness. Following solder plate for etch masking, the plating mask is stripped from the noncircuit areas. Etching is by a quick etch since only the electroless copper flash has to be removed. Consequently, copper waste may be less than 50%. After etching, operations such as solder stripping, tab plating and any other final fabrication methods are carried out as in the conventional subtractive process.

Table 1

Compositions and Operating Conditions for Brass Plating

Copper cyanide, g/L	32
Zinc cyanide, g/L	10
Sodium cyanide, g/L	50
Sodium carbonate, g/L	7.5
Sodium bicarbonate, g/L	10
Ammonia, m/L	2.5 - 5.0
pH	10.0 - 10.2
Temperature, °C	25 - 35

Source: Ref. #3

Table 2

Compositions and Operating Conditions for High Speed Brass Plating

Copper cyanide, g/L	75
Sodium cyanide, g/L	125
Zinc cyanide, g/L	5
Sodium hydroxide, g/L	45
Temperature, °C	45 - 75
Current density, A/m^2	108 - 861

Source: Ref. #3

Table 3

Compositions and Operating Conditions for Copper - Cadmium Bronze Plating

Solution:

-	Copper cyanide, g/L	30
-	Cadmium oxide, g/L	1.25 - 2.5
-	Sodium cyanide, g/L	45
-	Sodium carbonate, g/L	20

Operating Conditions:

-	Metallic copper, g/L	21
-	Metallic cadmium, g/L	1.1 - 2.2
-	Free cyanide, g/L	10
-	Temperature	room
-	Anodes	copper

Source: Ref #3

Table 4

Compositions and Operating Conditions for

Copper-Zinc Bronze Plating

Solution:

-	Copper cyanide, g/L	40
-	Zinc cyanide, g/L	3
-	Sodium cyanide, g/L	50
-	Rochelle salt, g/L	20

Operation Conditions:

-	Metallic copper, g/L	28
-	Metallic cyanide, g/L	1.7
-	Free cyanide, g/L	3
-	Anodes	Brass; 92% copper, 8% zinc
-	Temperature, °C	24 - 38
-	Current density, A/m^2	22 - 43

Source: Ref #3

Table 5

Compositions and Operating Conditions for

Copper-Tin Bronze Plating

Solution:

-	Copper cyanide, g/L	40
-	Potassium stannate, g/L	50
-	Potassium cyanide, g/L	90
-	Potassium hydroxide, g/L	15
-	Rochelle salt, g/L	60

Operating Conditions:

-	Metallic copper, g/L	28
-	Metallic tin, g/L	19
-	Free cyanide, g/L	27 - 30
-	Anodes	Forged, rolled or electrolytic copper
-	Temperature, °C	63 - 71
-	Current density, A/m^2	to 1076

Source: Ref. #3

Table 6

Compositions and Operating Conditions for Cadmium Plating Baths

	Alkaline Cyanide	Acid Fluoborate	Acid Sulphate	Neutral Sulphate
Ammonium chloride, g/L				11 - 22
Ammonium fluoborate, g/L		60		
Ammonium sulphate, g/L				75 - 110
Boric acid, g/L		27		
Cadmium, g/L	20	94		3.7 - 11
Cadmium fluoborate, g/L		240		
Cadmium oxide, g/L	22		7.5 - 11	
Sodium carbonate, g/L	30 - 60			
Sodium cyanide, g/L	100			
Sodium hydroxide, g/L	14			
Sulphuric acid, g/L			34 - 37	
Temperature, °C	15 - 38	21 - 38	15 - 32	15 - 38
Current density, A/m^2	54 - 970	320 - 640	100 - 640	22 - 160

Table 7

Composition and Operating Conditions

Chromium Plating Baths

	Decorative Plates	Hard Chromium	
CrO_3, g/L	250 - 400	250	400
H_2SO_4, g/L	2.5 - 4	2.5	4
Temperature, °C	38 - 43	55	50
Cathode current density, A/m^2	1250 - 1750	3100	2200

Table 8

Compositions and Operating Conditions for

Cyanide Copper Plating Baths

	Plain Cyanide	Rochelle Cyanide	High Efficiency
Copper cyanide, g/L	15	26	75
Sodium cyanide, g/L	23	35	93
Sodium carbonate, g/L	15	30	-
Sodium hydroxide, g/L	-	4	30
Rochelle salt, g/L	-	45	-
Free sodium cyanide, g/L	6	-	11
Temperature, °C	55	60	70
Cathode current density, A/m^2	220	430	650
Anode current density, A/m^2	80	160	270

Source: Ref. #5

Table 9

Compositions and Operating Conditions for

Copper Sulphate Plating Baths

	General Formulation	High Throw Bath
Copper sulphate, g/L	195 - 248	60 - 90
Sulphuric acid, g/L	30 - 75	172 - 217
Chloride, ppm	-	50 - 100
Proprietary additive	-	per vendor recommendation

Source: Ref. #5

Table 10

Compositions and Operating Conditions for

Copper Fluoborate Plating Baths

	High Concentration	Low Concentration
Copper fluoborate, g/L	450	225
Fluoboric acid, g/L	40.5	15
pH	0.2 - 0.6	1.0 - 1.7
Baume	37.5 - 39.5°	21 - 22°
Temperature, °C	18 - 66	18 - 60
Current density, A/m^2	1345 - 3767	807 - 1345

Source: Ref. #5

Table 11

Compositions and Operating Conditions for

Copper Pyrophosphate Baths

Copper pyrophosphate, g/L	52.5 - 84.0
Potassium pyrophosphate, g/L	201.1 - 349.1
Potassium nitrate, g/L	3.0 - 6.0
Concentrated ammonium hydroxide, ml/L	3.75 - 11
pH	8.0 - 8.7
Temperature, °C	43 - 60
Current density, A/m^2	1,000 - 8,000

Source: Ref. #3

Table 12

Compositions and Operating Conditions for Copper Pyrophosphate Baths for Printed Circuits

Copper pyrophosphate, g/L	57.8 - 73.3
Potassium pyrophosphate, g/L	231 - 316.5
Potassium nitrate, g/L	8.2 - 15.8
Concentrated ammonium hydroxide, ml/L	2.7 - 7.5
Addition agent	as required
pH	8.0 - 8.4
Temperature, °C	49 - 54
Current density, A/m^2	269 - 646

Source: Ref. #3

Table 13

Compositions and Operating Conditions for Iron Plating Baths

	Chloride	Sulphate	Double Sulphate	Sulphate Chloride	Fluoborate	Sulfamate
$FeSO_4 \cdot 7H_2O$, g/L		240		250		
$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$, g/L			250-360			
$Fe\ Cl_2.4H_2O$, g/L	300-450			35		
$Fe\ (BF_4)_2$, g/L					225	
$Fe\ (SO_3\ NH_2)_2$, g/L						305
$CaCl_2$, g/L	300					
NaCl, g/L					10	
NH_4Cl, g/L				20		
$NH_4SO_3NH_2$, g/L						30-40
pH	1.2-1.8	2.8-3.5	2.8-3.5	3.5-5.5	3.0-3.4	2.7-3.0
Temperature, °C	85	32-65	24-65	27-70	55-65	50-60
Current density, A/m^2	200-800	400-1000	200-1000	200-1000	200-900	500

Table 14

Composition and Operating Conditions of Lead Fluoborate Plating Bath

Lead fluoborate, g/L	337 - 412
Lead, g/L	195 - 239
Fluoboric acid, g/L	15 - 30
Boric acid, g/L	22.5 - 37.5
Peptone, g/L	4.5 - 7
pH	<1
Anodes	pure lead
Temperature, °C	21 - 38
Current density, A/m^2	215 - 753

Table 15

Composition and Operating Conditions

Nickel Plating Baths

	Watts Bath	Sulfamate Bath	Fluoborate Bath	All Chloride Bath
Nickel sulphate $NiSO_4.6H_2O$, g/L	225 - 413			
Nickel chloride $NiCl_2.6H_2O$, g/L	30 - 60	0 - 30	0 - 15	70
Nickel sulfamate $Ni(SO_3\ NH_2)_2$, g/L		263 - 450		
Nickel Fluoborate Ni (BF_4), g/L			225 - 300	
Total nickel as metal, g/L	58 - 107	62 - 113	58 - 79	17
Boric acid H_3BO_3, g/L	30 - 45	30 - 45	15 - 30	30
pH	1.5 - 5.2	3 - 5	2.4 - 4	~1.0
Temperature °C	46 - 71	38 - 60	38 - 71	~55

Table 16

Composition and Operating Conditions of Stannate Baths

Sodium stannate bath

	Rack	Barrel
Sodium stannate, g/L	90	180
Tin metal, g/L	40	80
Free sodium hydroxide, g/L	12	22.5
Temperature, °C	77-82	74-79
Cathode current density, A/m^2	161-215	54-161
Anode current density, A/m^2	269	161-269

Potassium stannate bath

Potassium stannate, g/L	100	200
Tin metal, g/L	40	80
Free potassium hydroxide, g/L	15	22.5
Temperature, °C	66-82	66-82
Cathode current density, A/m^2	323-1076	11-1076
Anode current density, A/m^2	323-431	108-323

Table 17

Composition and Operating Conditions

Zinc Plating Baths

	Barrel Plating	Still Tank or Automatic Plating	Conduit Tubing or Strip Plating
Zinc cyanide, g/L	60 - 83	60 - 83	60 - 90
Sodium cyanide, g/L	39 - 66	32 - 66	16 - 49
Sodium hydroxide, g/L	75 - 90	75 - 90	75 - 90
Sodium polysulfide,g/L	1.5	1.5	1.5
Temperature, °C	20 - 35	20 - 35	32 - 49

Table 18

Compositions and Operating Conditions for Cyanide Gold Plating Solutions

Gold, g/L	1 - 8
Free KCN, g/L	0.1 - 30
K_2HPO_4, g/L	15 - 30
K_3CO_3, g/L	0 - 30
pH	10 - 11.5
Temperature, °C	55 - 70
Cathode current density, A/m^2	1 - 10

Table 19

Compositions and Operating Conditions for

Indium Plating Baths

	High pH Cyanide	Sulphate	Fluoborate	Sulfamate
In as metal, g/L	15-30	20	72	20
$InCl_3$, g/L	30-35			
$In_2(SO_4)_3$, g/L		88		
$In(SO_3NH_2)_3$, g/L				70
$In(BF_4)_3$, g/L			235	
Dextrose, g/L	30-40			8
KCN, g/L	140-160			
KOH, g/L	30-40			
NaCl, g/L				45
Na_2SO_4, g/L		10		
H_3BO_3, g/L			20-30	
NH_4BF_4, g/L			40-50	
HSO_3NH_2, g/L				25
pH		2.0-2.5	1	0.0-0.2
Temperature, °C	20-30	20-30	20-30	20-30
Current density, A/m^2	150-300	200	100-1600	200-1000

Table 20

Compositions and Operating Conditions for Rhodium Plating Baths

	Sulphate (thin decorative)	Sulphate (heavy industrial)	Phosphate (thin decorative)
Rhodium as metal, g/L	2	5.25	2
H_3PO_4 (85%), g/L			55 - 115
H_2SO_4, g/L	50 - 160	50 - 100	
Anodes	Platinum	Platinum	Platinum
Temperature, °C	38 - 50	44 - 50	38 - 50
Current density, A/m^2	200 - 1000	1000 - 3000	200 - 1500

Table 21

Compositions and Operating Conditions for Silver Plating Bath

Silver as $KAg(CN)_2$	5 - 40 g/L
KCN (free)	12 -1 120 g/L
Potassium carbonate	15 g/L
Temperature °C	20 - 30
Current Density, A/m^2	11 - 431

TABLE 22

Compositions and Operating Conditions for Immersion Plating of Tin

On Aluminum

Sodium stannate	60 g/L
Temperature	79 - 82 °C

On Copper Alloys

1.	Tin chloride	25 g/L
	Sodium cyanide	25 g/L
	Caustic soda	3 g/L
	Temperature	Room
2.	Sodium stannate	8 g/L
	Sodium cyanide	16 g/L
	Caustic soda	1 g/L
	Temperature	21 - 66 °C

On Steel

1.	Stannous sulphate	1 - 3 g/L
	Sulphuric acid	7.5 - 20 g/L
	Temperature	82 °C to boiling
2.	Cream of tartar	120 g/L
	Tin chloride	5 g/L
	Temperature	Boiling

On Zinc

Tin chloride	170 g/L
Temperature	Room

TABLE 23

Sealing Techniques for Anodized Aluminum

Water Seal

Distilled or deionized water		
Temperature	=	95 - 100 °C
Time	=	30 minutes

Dichromate Seal

Potassium dichromate	=	100 g/L
Sodium carbonate	=	18 g/L
or		
NaOH	=	13 g/L
Temperature	=	90 - 95 °C
Time	=	2-4 minutes

Nickel/Cobalt Acetate Seal

Nickel acetate	=	5-5.8 g/L
Cobalt acetate	=	1.8 g/L
Boric acid	=	8-8.4 g/L
pH	=	5-6
Temperature	=	70 - 90 °C
Time	=	15-20 minutes

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APPENDIX C

DESCRIPTION OF WASTEWATER TREATMENT METHODS

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Table 1 Composition of Raw Waste Streams from Common Metals Plating
Table 2 Raw Wastewater Constituents from Printed Circuit Board Manufacturing

1.0 INTRODUCTION

Water is used for a multitude of purposes in metal finishing, including rinsing work pieces, washing away spills, air scrubbing, preparing process baths, and washing down equipment. However, approximately 90% of the volume of water used is for rinsing.

1.1 Wastewater Sources

Numerous sources contribute to the overall wastewater volume in a metal finishing facility. However, the most conspicuous source of pollution is the dragout of various processing baths into subsequent rinses. Dragout depends on several factors, for example the type of plating method and the configuration of the workpieces plated. Barrel plating dragout for instance is significantly higher per surface area processed than rack plating dragout. Smooth parts are likely to trap less process solutions than intricate parts, e.g. threaded fasteners.

Other noteworthy sources of pollution include discarded process baths and spent stripping solutions. However, plating baths and other process solutions containing high metal concentrations are rarely discarded; rather they are purified and reclaimed. If exhausted process solutions are beyond reuse, they can be handled in a number of ways. At some plants they are slowly metered into rinse waters following the operation and prior to treatment. Alternatively, these baths may be treated on-site in separate facilities or hauled away by waste contractors. Most cleaning solutions, for example, are handled by specialized waste disposal firms.

Spent stripping solutions, which arise from the salvaging of improperly plated parts, are usually handled the same way as other spent process solutions.

Consequently, although there are numerous sources of pollution at a metal finishing plant, in almost every case the most significant pollution problem is dragout and the resultant contaminated rinse water. For example, a study in the United States found the average rate of rinse water discharged from typical metal

finishing shops to be 18,500 gal/day (70,000L/day) whereas spent process solutions accounted for only 60 gal/day (230 L/day). Treatment of wastewaters at metal finishing plants is tantamount to treating rinse waters.

1.2 Wastewater Characteristics

The metal finishing industry utilizes a multitude of raw materials and virtually all of these find their way into the wastewaters at varying amounts. However, the pollutants of greatest concern appearing in the effluents are common heavy metals, hexavalent chromium, cyanide, toxic organics, total suspended solids, and oil and grease. Precious metals are usually recovered for their values and do not appear in any significant concentration in the effluent.

As mentioned, rinse waters comprise the largest volume of effluent; however, the concentration of pollutants is low. On the other hands, while spent process solutions are generally low in volume, their pollutant concentration is extremely high and should they be discharged into the rinse stream, the concentration of pollutants in the composite effluent stream can rise significantly. Typical characteristics of raw waste streams from common metals plating and printed circuit board manufacturing are depicted in Tables 1 and 2, respectively.

2.0 WATER CONSUMPTION REDUCTION

Significant reduction in water consumption can be achieved through careful design. Dragout minimization, effective rinsing, flow control and reusing contaminated rinse water and treated effluent are some common aspects of implementing water reduction measures. Raw wastewater reduction lessens the burden on water treatment facility. Effluent discharge reduction decreases the overall amount of contaminates released to the environment. Most water consumption reduction measures are simple and inexpensive to implement. The benefits for operators and the environment are significant. They should be implemented where possible.

2.1 Dragout Minimization

As workpieces are removed from plating solutions, some solution dragout stays on the surface of workpieces. These workpieces are rinsed to remove dragout and then the rinse water is treated. Thus one of the most effective methods of minimizing rinse water is to minimize the need for rinsing by reducing dragout. Dragout minimization techniques include:

2.1.1 Racking

Workpieces should be arranged so that each piece can effectively drain itself. Thus, cup-like area which will retain solution should face down, the longer dimension should be horizontal, and there should not be any stacking to allow effective draining. Design of parts and racks can greatly affect the amount of dragout and should be taken advantage of wherever possible.

2.1.2 Surface Tension Reduction

Surface tension is one of the determining factor of dragout. As surface tension is reduced, the force required to remove the solution from workpiece surface is reduced, and dragout is consequently minimized. Surface tension can be reduced by raising the temperature of the solution bath. Higher temperature also

decreases the kinematic viscosity of the dragout and thus increases the drainage rate. Use of wetting agents is another effective method of reducing surface tension.

2.1.3 Longer Withdrawal/Drainage Times

Longer withdrawal time can reduce the volume retained by the parts. Longer drainage time allows the retained solution to drain off more completely. They are both effective dragout minimization methods.

2.1.4 Low Concentration Plating Bath

Using lower concentration plating solution, less chemicals are carried out as dragout from the bath. Alternative solution e.g. non-cyanide zinc instead of cyanide zinc, which can give comparable finishings with lower plating solution concentration can significantly reduce dragout.

2.2 Effective Rinsing Method

The efficiency in dragout removal is dependent on the rinsing method used. Contact surface and flow pattern of rinse water are two features which affect the rinsing efficiency. Counterflow rinsing and spray rinsing are two commonly practised and proven methods.

2.2.1 Counterflow Rinsing

Counterflow rinsing introduces fresh water only to the last rinse tank. Overflow from one tank becomes feed to the rinse tank before it. The movement of the rinse water is opposite to that of the parts to be rinse, thus called counterflow rinsing. Effective rinsing is obtained in each rinse tank while fresh water required and wastewater to be treated are both minimized.

2.2.2 Spray Rinsing

The efficiency of rinsing is dependent on the contact surface on the parts by the water spray. Spray rinsing is particularly well suited for flat sheets. It is frequently the most efficient rinsing technique, since it removes significant amount of dragout with minimal amount of water.

2.3 Flow Control

Excess rinse water is often used due to lack of flow control. Flow control methods aid in adding only the amount of rinse water required.

2.3.1 Conductivity Cells

Conductivity cells provide effective control of rinse water in rinse tanks so that rinse water is replaced or made up only as required. The conductivity measures the conductance of the solution which is dependent on the ionic strength. As the rinse water becomes contaminated, the ionic strength increases and the conductance measurement increases. When the conductance reading exceeds a set point, the controller will allow makeup water to enter until the conductance reading drops below the set point. Since with conductivity cells water is only added when it is required and for the amount that it is required, significant reduction in water usage can often be achieved.

2.3.2 Flow Restrictors

Flow restrictors are installed to maintain a constant water flow in spite of water pressure fluctuations. It is particularly useful for constant production rate applications. It provides intermediate water usage control between manual and conductivity cell controls.

2.4 Reusing Contaminated Rinse Water and Treated Effluent

Internal system control is the first step in reducing water consumption. Various rinsing methods and controls cater to this purpose so that minimal amount of water is used. Reusing water is the next step in reducing overall water consumption. Rinse water may be reused treated or as is depending on the process and the solution. First rinse, which contains the most dragout, is often used as makeup water for the solution. It may be used untreated if evaporation of bath solution is significant; or it may require recovery treatment to concentrate the dragout before bleeding it into the bath.

Several water treatment methods can recover metal ions/salts, acids or other chemicals. The concentrate may be reused if it is pure enough. Problems may arise if the same rinse tank is used for different finishing processes on different surfaces. The concentrate from recovery processes will contain multiple metals or chemicals which may be hard to separate for reuse. The treated effluent, free of contaminants, can be reused as rinse water or makeup water instead fresh water. Treatment methods such as electrodialysis, electrolytic recovery, evaporation, ion exchange or reverse osmosis all can recover water. Some of them, e.g. reverse osmosis, are more suitable for recovering both water and concentrate than others, e.g. evaporation. A close looped water treatment setup uses and discharges minimal amount of water overall.

3.0 WASTEWATER TREATMENT METHODS

A wide array of processes are available to treat metal finishing effluents. Some of these simply remove or destroy the pollutants while other can recover process chemicals and water for reuse. At any particular site, the choice of treatment process or combination of processes will be dictated mainly by the volume and characteristics of the wastewaters, capital and operating costs involved, and prevailing environmental regulations.

The basic treatment system which has been adopted at many metal finishing plants is shown in Figure 1. As indicated, the various waste streams, particularly those containing hexavalent chromium and cyanides, are segregated and directed to appropriate treatment units. Cyanides are oxidized, usually by chlorine gas or sodium hypochlorite, and hexavalent chromium is reduced to the trivalent form to permit removal by hydroxide precipitation. The treated hexavalent chromium and cyanide wastes are then combined with metal-bearing streams from other sources and are treated with lime or sodium hydroxide to precipitate the metals. The precipitated metals are separated from the liquid stream in a clarification step. The liquid phase is discharged, usually to municipal sewers, while the collected sludge is thickened, dewatered and taken to an approved disposal site.

This type of treatment system is generally adequate for most metal finishing operations. However, if there are streams containing chelated metals, as is the case with electroless plating for example, then the chelated metals are also segregated and handled by other techniques such as sulfide precipitation since hydroxide precipitation is ineffective for chelated metals.

When waste streams containing significant amounts of oil and grease or toxic organics are present, then provisions have to be made for these also. Figure 2 is a flowsheet of treatment of various waste streams. Treatments of toxic organics and oily wastes will not be discussed in the following sections. The following sections are devoted to treatment methods for metal bearing wastewater.

3.1 Basic Treatment Methods

A basic treatment system for the metal finishing industry consists of cyanide destruction, hexavalent chromium reduction, metal precipitation and solids removal. Each step can be accomplished by one of the many methods.

3.1.1. Cyanide Destruction

Cyanides in the wastewater stream originate from dragout from plating baths. Some companies have switched to non-cyanide baths in view of the high toxicity of cyanide compounds. Others still feel cyanide baths give better finishings on products and continue to use cyanide baths. Rinse water containing dragout of plating bath has various cyanide concentrations. They can range from 1.4 mg/L to 256 mg/L in concentration. Cyanide exists mostly as ionizable cyanide or complex metal cyanide in the wastewater. Many methods for cyanide destruction have been used. Among these, chlorination is the most commonly used method.

3.1.1.1 Chlorination

Chlorine as chlorine gas or sodium hypochlorite is used in the chlorination process to oxidize cyanide.

The typical reactions using chlorine gas are as follows:

$NaCN + 2NaOH + Cl_2 \text{ ---> } NaCNO + 2NaCl + H_2O$

$2\ NaCNO + 5NaOH + 3Cl_2 \text{ --> } 6NaCl + CO_2 + N_2 + NaHCO_3 + 2H_2O$

If sodium hypochlorite is used; the reactions are as follows:

$NaCN + NaOCl \text{ ---> } NaCNO + NaCl$

$2NaCNO + 3NaOCl + H_2O \text{ --> } 3NaCl + N_2 + 2NaHCO_3$

In both cases, highly toxic cyanide is first oxidized to less toxic cyanate, then to nitrogen and bicarbonate.

Two stage oxidation is required since operating conditions for the two reactions are different. The pH and ORP measurements for the first stage oxidation from cyanide to cyanate are 10 - 10.5 and +300 to +400mv. Agitation and a retention time of 30 minutes are recommended. The second stage reaction is favoured at pH of about 8 and ORP measurement of +600 to +700 mv. Acid addition is required initially to lower the pH level of the cyanate wastewater. Cyanide destruction is often operated on batch basis for smaller plants. A two tank system with one for holding/equalization and the other for reaction is often utilized. Single reaction tank with a dividing baffle is also used for continuous operation.

3.1.1.2 Other Cyanide Destruction Methods

Other cyanide destruction methods include oxidation by ozonization, oxidation by ozonization with UV radiation oxidation by hydrogen peroxide, etc. These methods are rather uncommon.

Oxidation by Ozonization

Oxidation by ozonization can convert cyanide to cyanate as illustrated:

$$CN^{-1} + O_3 = CNO^{-1} + O_2$$

This treatment method is effective for zinc, copper, and nickel cyanides but ineffective for cobalt cyanide. Ozone is usually produced on-site by silent electrical discharge method. Capital investment and associated energy requirement are high with this treatment method.

Ozone dosage is the most critical operating parameter. It is dependent on the cyanide concentration in the waste stream. It can range from 1.0 mole ozone/mole CN for 20 mg/L of CN to 2.5 moles ozone/mole CN for 40 mg/L of CN. pH level of 9.0 - 9.5 enhances the operating efficiency.

Oxidation by Ozonization with UV Radiation

Ultraviolet radiation can be utilized in conjunction with ozonization to treat cyanide containing wastewater streams. The combination of ozonization and UV radiation enables more complex reactions at higher energy levels. Thus the energy required for ozonization with UV radiation is much less than ozonization alone. This combination is also more effective for some complex metal cyanides which can be resistant to ozonization alone.

Oxidation by Hydrogen Peroxide

Cyanides can also be oxidized to cyanates by heating, adding formalin (37% formaldehyde) and adding a hydrogen peroxide based solution. This technique is known as the Kastone Process. The following reactions take place:

$$CN^- + HCHO + H_2O = HOCH_2CN + OH^-$$
$$CN^- + H_2O_2 = NCO^- + H_2O$$

The operation proceeds as:

1. Heat cyanide containing wastewater stream to 49-54^{O}C. Adjust pH to 10.5 - 11.8.

2. Agitate the wastewater continuously add formalin.

3. Wait 2-5 minutes. Add hydrogen peroxide based solution.

4. Continue agitation for one hour. Reaction complete.

The high operating temperature and pH level allows the cyanide complex to break down to free cyanide ions for subsequent reactions. When the reactions are complete, cyanides are converted to cyanates while metal

ions are precipitated as oxides. This treatment method is particularly applicable to wastes from cyanide zinc and cyanide cadmium electroplating where recovery of metals are desired. Operating expenditures for this method include ongoing heating and chemical costs. Subsequent wastewater can cause a problem due to high BOD from formalin addition.

3.1.1.3 Other Methods

Electrochemical cyanide oxidation is well suited for treating high cyanide concentrations in the wastewater stream. It is relatively slow and less effective for waste streams containing less than 100 mg/L of cyanides. It does not require pretreatment, chemical addition, and subsequent treatment. It is also ineffective when sulphates are present in the wastewater stream. During this process, accumulated wastewater is pumped to a reactor where an applied DC potential oxidizes the free cyanide and cyanate to nitrogen, carbon dioxide and ammonia. The moderate capital investment and moderate operating cost is another advantage of the treatment method.

Precipitation of cyanide with ferrous sulphate to ferrocyanide is another treatment method which when accompanied by precipitation can effectively remove cyanides from the waste stream. It is usually used to remove iron cyanide from the waste stream.

Recovery of copper, zinc and cadmium cyanide with adsorption or other techniques is another alternative to cyanide destruction.

3.1.2 Hexavalent Chromium Reduction

Chromium exists mostly as hexavalent chromium in chromium containing wastes, generated in metal finishing processes. Hexavalent chromium is hard to segregate since its chromate is very soluble under all pH conditions. Trivalent chromium, on the other hand, is quite insoluble between the pH of 6 and 10. Therefore the most common hexavalent chromium treatment involves reduction

of hexavalent chromium to trivalent chromium then pH adjustment for precipitation and discharge.

3.1.2.1 Chemical Reducing Agent

The reduction process is mostly accomplished using sulphur bearing agents such as sulphur dioxide, sodium metabisulfite, or sodium bisulfite. The net reaction using sulphur dioxide as the reducing agent is:

$$3SO_2 + 2H_2CrO_4 + 3H_2O \rightarrow Cr(SO_4)_3 + 5H_2O$$

Ferrous sulphate can also be used but it generates additional sludge as iron hydroxide. The reduction of hexavalent chromium to trivalent chromium is favoured by low pH. And oxidation - reduction potential (ORP) measurement is used to monitor reducing agent addition. Thus continuous monitoring of pH at about 3, ORP at about +300 MV, appropriate agitation and a retention time of about 20 minutes can ensure a nearly complete reduction process.

Continuous systems and batch systems are both used for chromium reduction. In general, batch systems are used for small flows while continuous systems are used for flowrates of 110 L/min and over.

After reduction, an alkaline such as sodium hydroxide is added to the trivalent chromium bearing stream to raise the pH to about 8.5. Precipitation, sludge separation, sludge dewatering, and wastewater discharge can be done accordingly at this pH.

3.1.2.2 Electrochemical Reduction

Consumable iron electrodes and an electrical current to generate ferrous ions can be used to reduce hexavalent chromium to trivalent chromium. The reaction is as follows:

$$3Fe^{+2} + CrO_4^{2-} + 4H_2O \rightarrow 3Fe^{+3} + Cr^{+3} + 8OH^-$$

The reduction reaction occurs readily to reduce hexavalent chromium concentration to less than 0.05 ppm in the effluent. The ferric and trivalent chromium ions will precipitate as hydroxides between the pH of 6 and 9.

If the raw wastewater is low in pH, neutralization/precipitation stage will effectively segregate the metal ions as metal hydroxides. The iron electrodes require daily cleaning with dilute acid solution to function efficiently. New electrodes are also needed periodically as they deplete.

3.1.2.3 Other Methods

Hexavalent chromium can be precipitated by iron sulfide. It can also be removed from the waste stream by an anion exchanger. These methods are discussed in precipitation and ion exchange sections respectively.

3.1.3 Solids Removal

Solids can be removed by the waste stream by various methods. Filtration and gravity settling are two examples. For both methods, a neutralization/precipitation stage is often first exercised.

3.1.3.1 Neutralization/Precipitation

Neutralization is required for acidic and alkaline wastewater streams prior to discharge. It is often accomplished with precipitation after other treatments. Currently the regulated pH range for wastewater discharge to sanitary sewers is 6 to 10.5. Metal salts are often precipitated as pH is adjusted. Since different metals have different solubilities at different pH, the ideal pH often depends on the metal salts targeted in the wastewater stream. Most heavy metals have high solubility at low pH, thus the pH range of 7.5 to 9.5 is generally monitored for precipitation.

Other agents and/or parameters can be used to precipitate metals. The following are some common methods:

1) The chemicals most frequently used for precipitation of metals are lime, caustic soda (NaOH), and sodium carbonate. Due to its lower cost, lime is generally preferred. Sodium hydroxide is sometimes used in small installations where daily chemical costs are not significant. Soda ash, i.e. sodium carbonate, is employed in particular cases (e.g. nickel and cadmium removal) where it provides a superior precipitation.

   The pH at which minimum solubility occurs varies for each metal. When more than one metal is present, the pH must be selected which optimizes the removal of all the metals. The minimum solubility for the common heavy metals occurs from pH 7 to 10.

   Hydroxide precipitation, the most common method, is generally effective in removing heavy metals down to 1 ppm or less. However, a major limitation of the hydroxide precipitation method is the inability to precipitate complexed metals. In such cases, other precipitation methods must be used.

2) Sulfide Precipitation: Chemical precipitation by hydrogen sulfide or a soluble sulfide salt such as ferrous sulfide is effective in precipitating simple and complexed metals in the wastewater stream. At alkali pH levels, most metal sulfides have lower solubilities than metal hydroxides. With ferric sulfide as reducing agent and a pH between 8 and 9, even hexavalent chromium can be precipitated as chromium hydroxide.Sulfide precipitation is also advantageous over hydroxide precipitation because it is insensitive to the presence of most chelating agents. Thus all wastes can be treated together. However, pH control and proper ventilation is essential since excess sulfide produce gaseous hydrogen sulfide as a co-product. Excess solids are generated from use of ferric sulfide as ferric ion precipitates.

3) High pH precipitation is used for treating complexed metal wastes. It involves adding a chemical such as calcium hydroxide to the wastewater to raise the pH thus prompting complexed metal ions to dissociate to uncomplexed ions. The uncomplexed ions can then be precipitated with

available hydroxide ions. The effectiveness of high pH precipitation is dependent on the complexing agent and pH control. For example, high pH precipitation for complexed copper ions with calcium hydroxide is enhanced with complexing agents containing carboxyl groups but ineffective with complexing agents containing no carboxyl groups and only hydroxyl groups.

4) Chemical Reduction/Low pH Precipitation

Another method for breaking up complexed metal ions is to lower the pH of the waste stream to about 4 with a chemical agent such as dilute sulphuric acid. A reducing agent such as sodium hydrosulfite is added to lower the oxidation state of the ions. After reduction, pH is raised with another chemical (e.g. lime) to about 9 to precipitate the metal ions out of the waste stream. Waste stream from printed circuit board manufacturing is sometimes treated in this fashion. Chemical precipitation generates a large quantity of metal containing sludge which then has to be appropriately disposed.

3.1.3.2 Gravity Settling/Sedimentation

Gravity settling is a process by which the waste stream is slowed down to allow effective settling and removal of solid particles in the waste stream. Equipments ranging from lagoons, conventional clarifiers to improved clarifiers (e.g. inclined plate) can all be effective for solid settling. Depending on the solid particles to be removed and whether a lagoon or an inclined plate clarifier is used, retention time can range from 1 to 48 hours for effective settling. Improved clarifiers require less time and have higher efficiency than conventional clarifiers than lagoons or tanks. Clarifiers requires higher capital investment while lagoons and tanks require a large space. Therefore the ultimate equipment is selected based on specific needs and circumstances at each plant.

3.1.3.3. Filtration

Filtration is a process by which the waste stream is passed through certain filtering media to cause separation of the waste stream. It often follows

precipitation and solid settling to remove the remaining solids in the waste stream. Depending on the filtering media, suspended solids of different sizes and types can be retained by the media. The following are some examples of different filtering technologies used in the metal finishing industry.

Granular Bed Filtration

Granular bed filtration utilizes a bed of single or multi-media filters through which the waste stream is passed through by gravity or by pressure. There are many variations of granular bed filtration. They can differ in filtration rate, filter media, flow pattern, method of pressurization or method of cleaning filter media.

In filtration rate, granular bed filters are traditionally classified into slow sand, rapid sand and high rate mixed media. As filtering rate goes up, hydraulic loading and frequency of filter cleaning increases. More automated cleaning method, such as backwashing, is often utilized with high rate filters.

In filtering media, granular bed filters can have single, dual or mixed media filters. Single media filters are effective but dual and mixed media filters allow higher flow rates and efficiencies. Dual and mixed media filters usually consist of coarser and less dense media at the top and finer and denser media at the bottom. The coarse material such as coal will remove most of the solids in the influent while the finer material such as sand can retain the finer suspended solids.

The flow pattern is usually top-to-bottom although bottom-to-top, horizontal, and bi-flow are sometimes used. In bottom-to-top pattern (upflow backwash), the filter media (coarse-to-fine) is maintained in the corresponding top-to-bottom order. But filtration efficiency may suffer in this flow pattern as filter bed becomes fluidized. In a bi-flow filter, inlet flow enters through both top and bottom and exits laterally.

Granular bed filters mostly operate by gravity. However, pressure filters permit higher solid loadings before cleaning and can often be desirable for the system.

Filter media can be cleaned manually by scraping as in a single media, slow sand filter. Other methods such as surface wash and backwash are also used. Surface wash employs water jets just below the surface. It is often used as an auxiliary cleaning method to enhance solids removal in the upper few inches of filter beds. Backwashing is accomplished by pumping water opposite to the usual flow pattern and thereby releasing the solids retained in the media.

Membranes Filtration

Membrane filtration utilizes continuous recirculation of wastewater through a tubular membrane filter module. Typically wastewater is pretreated and pH adjusted prior to membrane filtration. Some chemical addition to cause the metal precipitate to be non-gelatinous, easily dewatered and highly stable is required. As the treated wastewater is continuous recirculated through the membrane filter, water and any dissolved salts permeate the membrane leaving the slurry behind. When the solids concentration in the slurry reaches 10 to 15%, it is pumped out and disposed as sludge.

Membrane filtration features easy installation to most end-of-pipe conventional system, adoptability to pollutant input and a stable alkaline sludge. However, careful pH monitoring, frequent membrane cleaning and/or replacing are essential for effective operation of membrane filtration.

3.2 Advanced and Other Treatment Methods

Other effluent treatment methods which have become established in the metal finishing industry include evaporation, reverse osmosis, ultra filtration, ion exchange, electrodialysis, electrolytic recovery and destruction, and adsorption. Detailed description of these and other applicable technologies along with case studies illustrating their use have appeared in several books and a vast multitude of other publications. For example, each year there are numerous of citations in such abstracts as Chemical Abstracts, Pollution Abstracts, Metal Abstracts etc. Annual review issues in such periodicals as the Journal of the Water Pollution Control Federation and Metal Finishing also describe proven and emerging technologies and their applications. Moreover, pollution control journals and

other journals devoted to the metal finishing industry frequently carry articles, new technologies and products involving various aspects of waste treatment. Numerous government publications, particularly by the US EPA, are also an excellent source of information on technologies for handling metal finishing wastewaters and sludges.

The General Bibliography at the end of this section lists some of the most useful publications pertaining to metal finishing wastes. Described below in some details are the various techniques for minimizing water consumption, treating wastewaters, and managing sludges in the metal finishing industry.

3.2.1 Electrodialysis

Electrodialysis (ED) utilizes an electrical driving force over a series of ion exchange membranes. An electrodialysis unit usually has many membrane cells stacked up in parallel. Each membrane cell has a cation exchange, or anion exchanger and several membrane spacers. The anion exchangers and cation exchanges are arranged alternatively and membranes are selectively permeable to anions or cations. Anion exchange membrane allows anions to pass through while cations exchange membranes are permeable to cations. As wastewater is pumped through the electrolysis unit cations are drawn to anodes and anions are drawn to cathodes. The resulting effluent water is low in ions while ions are concentrated in the compartments.

Electrodialysis is a relatively new waste treatment method in the metal finishing industry. It is generally used for treating rinse tanks, particularly first rinse, to minimize build-up. Electrodialysis produces higher concentrate than reverse osmosis. Electrodialysis, even with stacked up units, is only partially effective in removing contaminants. It is generally not economically feasible for treating very dilute rinsewater. Other treatment methods are required before final effluent is discharged.

3.2.2. Electrolytic Recovery

Electrolytic recovery utilizes an electrolytic cell within which metal ions in the wastewater are deposited onto the cathode as elemental metals and oxygen is produced at the anode. Recovery of metal ions using electrolytic recovery typically has a drag-out recovery tank before the electrolytic recovery tank and a recirculating pump. It produces high purity metal foil or powder which has a high resale or reuse value. More than 90% recovery efficiency has been claimed in the advanced electrolytic cell design systems.

Conventional electrolytic recovery uses stainless steel cathodes. It is only effective in recovering metals in high concentrations. Agitation can enhance recovery efficiency. Advanced electrolytic recovery such as Dupond's extended surface electrolysis recovery system recovers better in low concentration than in high concentration. This system utilizes a spiral cell which consists of a cathode made out of stainless steel mesh, a porous insulating separator, an anode, and another separator. The cell with the above components rolled-up to a spiral shape has a very high porosity. It can be used alone or stacked up as modules for more thorough recovery. Periodic interruption to clean deposited metals off cathodes with and cleaner is required.

The Chemlec cell is another advanced electrolytic recovery method. It consists of a set of apertured expanded meal-mesh electrodes which are immersed in a bed of small glass beads. The glass bead bed is kept fluidized by pumping rinsewater through the bed in an upward direction. The electrodes are most commonly titanium but mild steel is also used for treating alkaline cyanide solutions. The Chemlec cell features good agitation by the glass beads and a removable cathode. As the cathode mesh is covered with deposited metal, it is removed to be cleaned off or used as an anode in the plating bath.

The High Surface Area (H.S.A.) system collects metals from still rinse bath on its carbon filament mats cathode. The build up metal is removed electrochemical or chemically and returned to the bath. This Canadian System has demonstrated 98% removal efficiency at a commercial facility.

An added benefit of this method is that cyanides are destroyed via oxidation in this process thus elimination the necessity for pretreatment.

3.2.3 Evaporation

Evaporation can be used in the metal finishing industry for recovery of metals, bath concentrates and rinse water. However, high energy cost is associated in operating it.

Both atmospheric and pressure evaporation are available. A packed column evaporator with an accumulator bottom and a heat exchanger is generally used for atmospheric evaporation. Wastewater is pumped through heat exchange and sprayed on the packing from the top of the column. At the same time, hot air is blown through the packing from the bottom of the column and carry off the moisture as it contacts the partially vaporized liquid. When wastewater is evaporated, water vapour may be condensed and recovered while solute is concentrated in the solution. A condenser and additional piping will be required, if water vapour is to be recovered and reused.

In vacuum evaporation, vacuum condition is maintained to allow reduced temperature for boiling the liquid. Submerged tube evaporator is most widely used. Wastewater is accumulated at the bottom of the vessel where submerged stream coils evaporate it. As the water vapour rises up and contacts the cooling coils, it condenses and the condensate is collected in a trough. A vacuum pump maintains the desired pressure in the enclosed vessel. Other vacuum evaporators such as climbing film evaporator and and double-effect evaporator also exist.

Pretreatment of wastewater such as solids removal and pH adjustment is generally required to minimize corrosion, scaling and clogging in the evaporator and associated equipments. If a closed-looped recovery system is used, a cation exchanger is required to remove the impurity build-up. Otherwise, dissolved metallic impurities can build-up to foul the system.

3.2.4 Ion Exchange

Ion changer is a versatile technology which is effective and efficient in removing a wide range of metals from the waste stream. It is particularly attractive, costwise, for treating large flows with low contaminant concentration.

The treatment is accomplished by passing wastewater through a resin bed. There are basically two types of resin, cation resin and anion resin. Cation resin removes cations (e.g. metal ions) and anion resin removes anion, (e.g. dichromate). There are a wide range of resin with different properties such as ionization strength and selectivity for specific metal ions. The wastewater usually pass through a filter to remove solids, a cation exchanger, and then a anion exchanger. A second pass by recycling or a second unit in series is sometimes used to achieve higher removal of contaminants.

As harmless ions held by electrostatic forces in the resin are exchanged for targeted ions in the waste stream, the resin becomes saturated. Spent resin can be replaced/disposed, sent off-site for regeneration (usually back to the resin supplier), or regenerated on-site. Regenerating resin on-site requires either a shut-down period or multiple ion exchangers hooked up in parallel. Cation resin is usually regenerated with hydrochloric acid or sulphuric acid while anion resin is regenerated with sodium hydroxide. After regenerating, the regenerating agents contain concentrated targeted material of the wastewater. This ability to concentrate is sometimes desirable for recovery purposes. Otherwise, the contaminated regenerating agents will have to be treated in the system.

Ion exchange is used in the metal finishing industry for chemical recovery, water recycle, and effluent polishing.

3.2.5 Reverse Osmosis

Reverse osmosis (RO) separates solute from a solution by forcing the solvent through a membrane by applying a pressure greater than the normal osmotic pressure. RO generally refers to processes where the solute and solvent molecular sizes are comparable. This separation process produces a concentrate and a permeate on opposite sides of the membrane for reuse or separate disposals.

RO has been found successful in recovering Watts-type nickel, nickel sulfamate, copper cyanide and many other plating solution from rinsing water. It can be designed as a closed-loop system with plating bath and counter-current rinsing. The first rinse is routed to the RO system and after separation the concentrate is returned to the plating bath while the permeate is returned to the last rinse. Modules with different mechanical and structural arrangements are commercially available. With careful selection of the membrane, it is effective in separating a wide range of solids from the wastewater stream under a wide pH range. RO is also relatively inexpensive to operate and requires little floor space. However, RO has a narrow optional operating temperature range. The membrane is also susceptible to chemical attacks by strong acids and bases, and fouling by suspended solids or gelatinous material.

3.2.6 Adsorption

Many natural and synthetic materials have the ability to adsorb various forms of metals and/or cyanides from wastewaters and hence are utilized for pollution control. Included among these are activated carbon, synthetic polymeric resins (such as these marketed by the Rohm and Haas Co.), clay, and various wastes and discards (e.g. rubber, agricultural residues, wood, straw and the like).

Generally speaking, the basic problem with most adsorbents is the amount of uptake of pollutants and the regeneration of the sorbents materials. Most adsorbents are not very efficient in removing metals, i.e. the amount removed per unit weight or volume of sorbent is low.

If the sorbent cannot be regenerated, then the metal-contaminated sorbent must be disposed of. Even if the sorbent can be effectively regenerated, the metal-contaminated regenerate solution still has to be treated or disposed of.

A novel sorbent method which is very efficient and readily regenerable is the DeVoe-Holbein technology which utilizes coordinating compounds covalently bonded to the surface of an inert material to capture metal ions. Removal rates of 99% or higher are possible. Moreover, only a small volume of regenerant is required to restore the sorbent to its original capacity. This technology has been successfully demonstrated for the removal of a variety of metals from typical metal finishing effluents. Spent regenerant is handled similarly to ion exchange regenerant solutions.

3.2.7 Crystallization

Crystallization occurs in a supersaturated solution where the difference between the concentration of the feed and the solubility of the solute causes formation of small solute particles. In order for this technology to be applicable, the concentration of the target salts in the rinsewater has to be relatively high. Therefore, the process may require some adjustments to slow down the operation and rinsewater flowrate so that the salt concentration will increase.

This recovery method has been demonstrated in the printed circuit board manufacturing industry. The etching bath in the PC board manufacturing industry does not contain ammonia or chelating agents, and the slower etching reaction enables continuous crystallization of metal salts. The metal salts may be sold as by-products or the metal content may be recovered electrolytically for reuse.

3.2.8 Starch Xanthate

Starch Xanthate is a process developed by Dr. Robert Wing of the U.S. Department of Agricultural. The process utilizes polymeric poly-xanthates such as starch xanthate in the presence of cationic polymers. The starch xanthate reported can replace heavy metal ions in the rinsewater much like an ion exchanger. The final starch xanthate sludge reported require acid or heat treatment to recover metals.

The technology has been investigated in one commercial establishment. Good removal of copper, iron, zinc, tin and lead was reported. Recovery of starch xanthate was not investigated at this facility.

4.0 SLUDGE MANAGEMENT

Sludge streams generated from water treatment generally range from one to five percent solids. They are bulky and costly to dispose of in this state. Several dewatering methods/treatment techniques are available to remove excess water and produce a thicker sludge of up to thirty five percent solids. The following are some representative methods:

4.1 Centrifugation

Centrifugation force can be used to concentrate the sludge. Separation between immiscible liquids of different densities (e.g. chemicals, metallic ion bearing water, etc.) or solids and liquids are both possible with centrifugation. All centrifuges operate on the same centrifugal force but varying discharge setup. There are three types of centrifuges used in the waste treatment field i.e. disc-nozzle (disc), imperforate basket (basket) and solid bowl - conveyor (conveyor). Both disc and conveyor types are continuous while basket type is batch-operated.

In the disc centrifuge the raw sludge enters at the top and is distributed between channels which act as spacers in conical discs. As concentrated solids flow down the channel, they are flushed out continuously with part of the wastewater. The effluent is discharged through separate overflow weirs.

The basket centrifuge does not have continuous solids discharge. Raw sludge is fed to the bottom of the centrifuge for a preset time or until the concentrate reach a preset concentration. Effluent can overflow through the top for discharge during this period. When centrifugation slows down to about 70 RPM, plowing then begin to remove the solid build-up. Centrifugation resumes when plowing is completed.

The conveyor type centrifuge has a rotating horizontal bowl with a screw conveyor. Sludge enters the bowl through a stationary feed pipe. Solids which

settled on the wall of the bowl under centrifugal forces are carried out by the screw conveyor. Effluent is discharged through ports in the bowl.

Sludge dewatering with centrifugation has relatively low initial capital cost but high operating energy cost. Centrifugation is a widely used technique for its reliability and ability to handle a wide range of sludge types. Some conditioning of sludge by polymer addition may be required.

4.2 Gravity Sludge Thickening

Gravity thickening is accomplished in two stages. Sludge is fed into a thickener tank where racks stir the sludge to allow settling. Then in a secondary clarifier the solids are allowed to settle by gravitational force. Solids collected at the coned shaped clarifier bottom are pumped out periodically. Effluent is discharged as it overflows weirs at the top.

Gravity thickening is generally used as a pre-dewatering volume reduction technique. It is relatively low cost and easy to maintain. However, it is sensitive to feed rate. Too high a feed rate will disturb the settling process. The final solid content by gravity thickening will never exceed 12%.

4.3 Pressure Filtration

Pressure filtering filters sludge through a filter media and enhances the cake by creating a pressure on one side. Filter media which is impermeable to solids is rigidly fixed by several plates in a frame. When sludge is pumped under pressure to the press, liquid quickly passes through the filter media to discharge while the solids are retained. Two types of filter pressures are used in sludge dewatering; fixed volume recessed plate filter press and variable volume recessed plate filter press (diaphragm filter press).

In a fixed volume recessed plate filter press, sludge is pumped to the press, enclosed with filter media at both ends, at high pressure. When solid build-up causes filtration to be unproductive, pumping is stopped, solids are cleaned off and the cycle restarts. In a diaphragm filter press, sludge is pumped through the

press at low pressure. As solids build up to stop effective filtration the diaphragm is inflated to further remove water and to allow solid removal.

Pressure filtration filters have short lift span and must be replaced from time to time. Most pressure filtration presses are not automated thus quite labour intensive. These factors contribute to high operating cost. However, pressure filtration produces a very dry cake which can sometimes reach 35% in solids. It is therefore desirable if maximum dewatering is desirable for subsequent solids landfilling or incineration.

4.4 Sludge Bed Drying

Sludge can be dried by draining (gravitation) and evaporation by sludge bed drying. Sludge is distributed in drying beds which are divided into sections. The beds usually have a layer of sand over a layer of gravel over drain tiles. Roofing is sometimes desirable over the beds.

Where large spaces are available, sludge bed drying can be an inexpensive, and low maintenance way to get rid of excess of water in the sludge. Periodic removal of sludge and sand is the major upkeep. Adequate drying often requires a lengthy period of time. A high solid content can eventually be achieved. Special care must be taken to ensure proper drain tiles design so that leachate will not be a problem later on.

4.5 Vacuum Filtration

Vacuum filtration is usually accomplished by a rotating cylindrical drum partially submerged in a sludge bed. The cylindrical drum is vacuum and a filter media exterior. In the submerged section, vacuum drains some sludge towards the cylinder. The water is drawn through while the solids are retained on the filter media. As the cylinder rotates, the solids dry in the air and then drops to a hopper.

Vacuum filtration has a high initial cost but low operating cost. Filter media upkeep/replacement and energy are the two major operating costs. Vacuum

filtration requires a minimal solid content e.g. 3% for adequate cake formation. The ultimate solids content can reach up to 30%.

4.6 Ultimate Disposal

Metal-contaminated dewatered sludges are most often disposed of in approved landfill sites. At some of these facilities, the sludges are mixed with an inert material (e.g. sand) or certain chemicals or are solidified prior to burial.

Sludges can also be processed to recover metals. However, although recovery can be accomplished by a variety of methods, it is seldom economical unless precious metals are involved or unless only one metal is present in relatively significant amounts. Sludges containing a mixture of common metals are generally not worthwhile to process for recovery.

Sludges can also be incorporated into such products as building or road construction materials; but this alternative is likewise seldom practised.

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Table 1

Composition of Raw Waste Streams from Common Metals Plating

	mg/L
Copper	0.032 - 272.5
Nickel	0.019 - 2954
Total Chromium	0.088 - 525.9
Hexavalent Chromium	0.005 - 334.5
Zinc	0.112 - 252.0
Total Cyanide	0.005 - 150.0
Fluoride	0.022 - 141.7
Cadmium	0.007 - 21.60
Lead	0.663 - 25.39
Iron	0.410 - 1482
Tin	0.060 - 103.4
Phosphorus	0.020 - 144.0
Total Suspended Solids	0.100 - 9970

Table 2

Raw Wastewater Constituents from Printed Circuit Board Manufacturing

Constituent	Range (mg/L)
Total suspended solids	0.998 - 408.7
Cyanide, Total	0.002 - 5.3
Cyanide, Free	0.005 - 4.6
Copper	1.582 - 535.7
Nickel	0.027 - 8.4
Lead	0.044 - 9.7
Chromium, Hexavalent	0.004 - 3.5
Chromium, Total	0.005 - 38.5
Fluorides	0.648 - 680.0
Phosphorus	0.075 - 33.8
Silver	0.036 - 0.2
Palladium	0.008 - 0.10
Gold	0.007 - 0.19

FIGURE 1 - BASIC TREATMENT SCHEMATIC

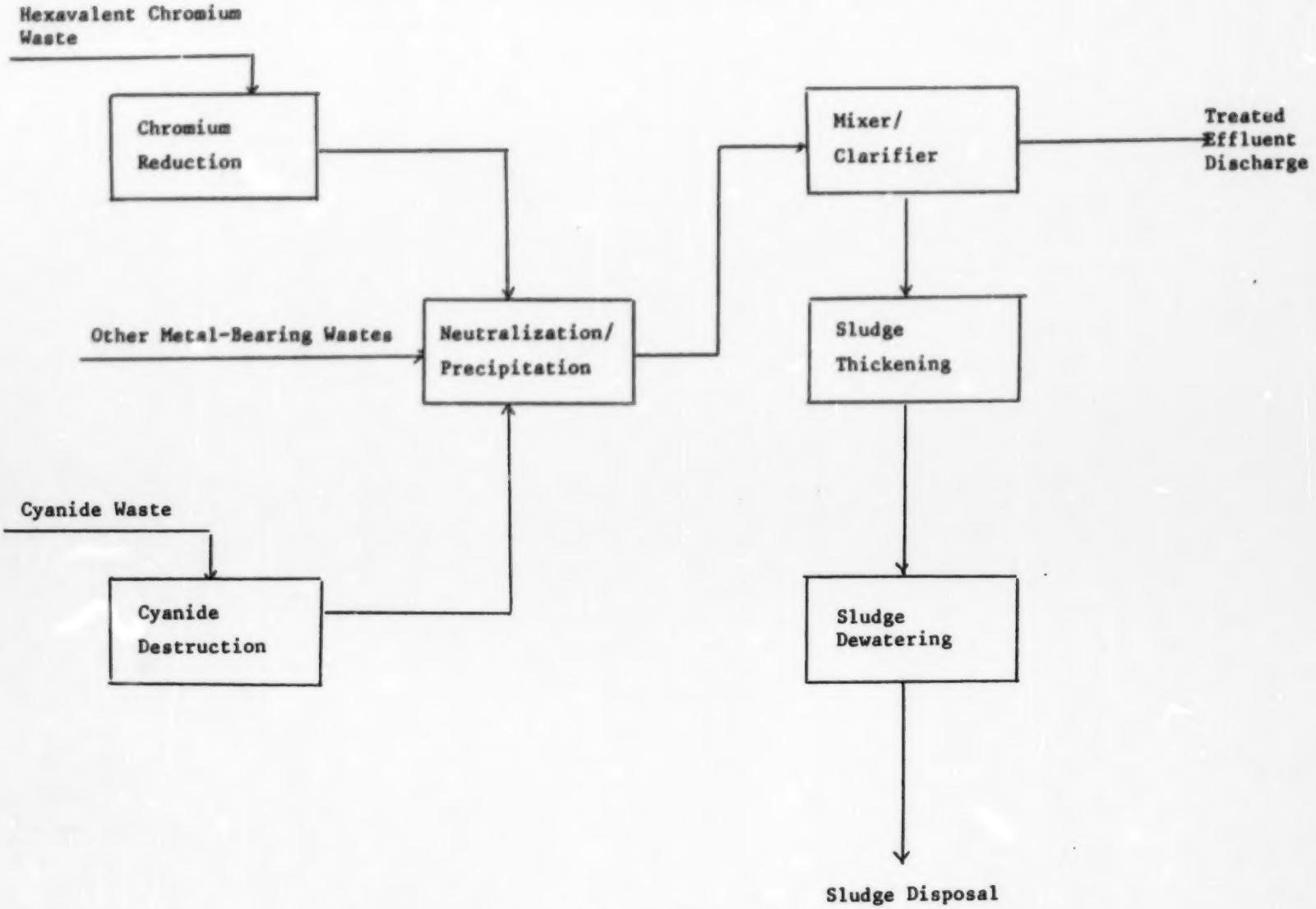
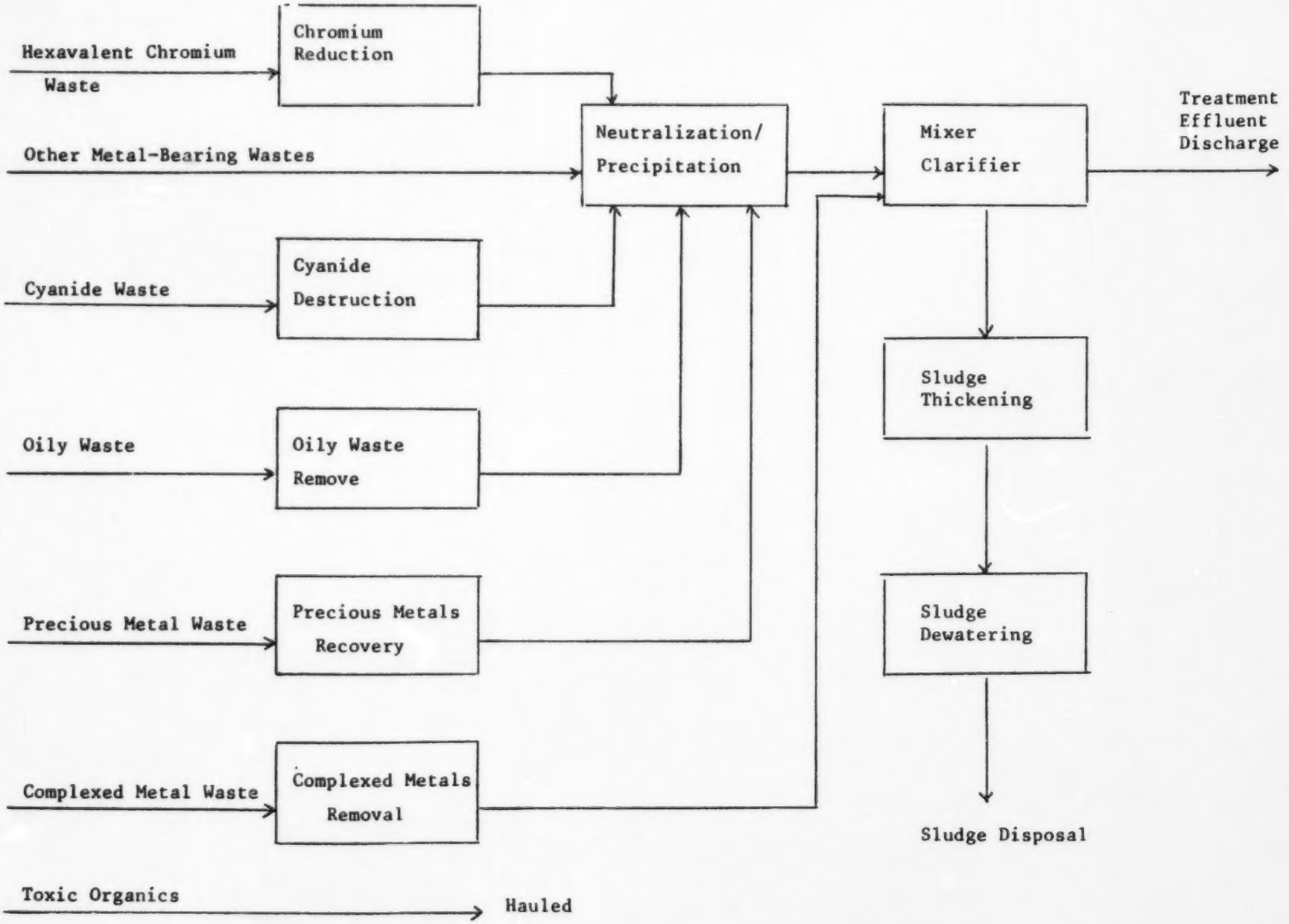
FIGURE 2 - COMPLEX TREATMENT SCHEMATIC